Volume 28 DECEMBER, 1958 Number 4

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Journal of Sedimentary Petrology

A Publication of the Society of Economic Paleontologists and Mineralogists
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« CONTENTS »

Depositional environment of the Ordovician succession in the Marathon region, Texas ..... *William B. N. Berry* 389

Tidal action as a cause of clay accumulation ..... *L. M. J. U. van Straaten and Ph. H. Kuenen* 406

Fresh-water environment of deposition of Precambrian banded iron formations ..... *J. L. Hough* 414

Occurrence of alkali metals in some Gulf of Mexico sediments ..... *Charles W. Welby* 431

Displacement of microfossils ..... *Daniel J. Jones* 453

Techniques in sedimentary geochemistry: (1) Separation of the detrital and non-detrital fractions of limestones ..... *D. M. Hirst and G. D. Nicholls* 468

"Size factors," a means of analysis of data from textural studies of till ..... *Vincent C. Shepps* 482

Corrosion zones: a modified hypothesis of their origin ..... *Malcolm P. Weiss* 486

Notes on diagenetic dolomitization ..... *Harold J. Bissell and George V. Chilingar* 490

Coprolites: a review of the literature and a study of specimens from southern Washington ..... *G. C. Amstutz* 498

Settling tube for mechanical analysis by decantation ..*N. Prokopovich* 509

DISCUSSIONS

Problem of the origin of fine-grained gypsum, "Superindividuals," and selenite in gypsum rock ..... *Marcus I. Goldman* 510

"Dolostone" ..... *A. Vatan* 514

NOTE

Modification of underwater surface sediment layers by sea mussels (*Mytilus edulis*) ..... *R. L. McMaster* 515

ANNOUNCEMENTS 517

INDEX 519

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Corprolites: a review of the literature and a study of specimens from southern Washington ..... *G. C. Amstutz* 498

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DISCUSSIONS

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"Dolostone" ..... *A. Vatan* 514

NOTE

Modification of underwater surface sediment layers by sea mussels (*Mytilus edulis*) ..... *R. L. McMaster* 515

ANNOUNCEMENTS 517

INDEX 519

PAPERS IN PRESS FOR FORTHCOMING ISSUES

Geology and paleontology of Norwegian sea bottom cores. By H. Holtedahl.

Playa deposit in the Bishop's Lodge Member of the Tesuque Formation, Santa Fe County, New Mexico. By W. W. Boyer.

Small scale cross-lamination in limestones. By J. W. Harbaugh.

Evidence of transgressive-regressive Cambrian sandstones bordering Lake Superior. By E. G. Driscoll.

Clay mineral composition of some recent marine sediments. By K. Oinuma, K. Kobayashi, and T. Sudo.

Sediments from Danish lakes. By K. Hansen.

Analysis of interlayer mixtures of three clay mineral types by X-ray diffraction. By E. C. Jonas and T. E. Brown.

Insoluble residue—magnesium content relationship of carbonate rocks from the Devonian Cedar Valley Formation. By R. Bisque and J. Lemish.

The slotted cone splitter. By F. J. Flanagan, R. C. Kellagher, and W. L. Smith.

Identification of carbonate minerals by staining methods. By G. M. Friedman.

A photomultiplier photometer for studying quartz grain orientation. By A. L. Pierson III.

New method for study of calci-phosphatic pellets. By P. Tasch.

JOURNAL OF SEDIMENTARY PETROLOGY, VOL. 28, NO. 4, PP. 389–405
FIG. 1, PLATES 1–4, DECEMBER, 1958

DEPOSITIONAL ENVIRONMENT OF THE ORDOVICIAN SUCCESSION IN THE MARATHON REGION, TEXAS[1]

WILLIAM B. N. BERRY
University of California, Berkeley, California

ABSTRACT

Graptolites occur primarily in limestones in the Ordovician succession in the Marathon region. Study of thin sections of these limestones reveals that most of them were lime muds; however, oölitic and bioclastic limestones also bear graptolites.

Integration of the thin section study of the several rock types occurring in the Ordovician sequence with analysis of the associated sedimentary features enables recognition of four major environments. During the Early Ordovician mud was accumulating in the region. Local sectors of it were frequently exposed for brief periods; also, for a short time, small patch reefs flourished. In the early part of the Middle Ordovician strong currents swept the area and calcium carbonate oölites and aggregates formed. Aligned biserial graptolites and the direction of dip of the cross-laminae indicate that the last current to pass over the region came from the southwest. Then a tidal mud flat developed during the latter part of the Middle Ordovician. It was occasionally swept by currents bearing pelagic organisms. Aligned biserial graptolites again indicate that the direction from which the current came was southwest. Finally during latest Middle Ordovician and all of the Late Ordovician the region was predominantly accumulating lime mud under reducing conditions.

INTRODUCTION

While studying the Ordovician graptolite faunas of the Marathon region of Texas the nature of the rocks in which the graptolites were found posed an interesting environmental problem. The Marathon region graptolites consitutute the most extensive graptolite fauna to be described from limestones. Although shale and chert compose more than 60 percent of the Ordovician section, the limestones bear most of the graptolites and all of the better-preserved specimens. Because the classic conception is that graptolites occur in black shales, a detailed examination of the nature of these graptolite-bearing limestones was undertaken. Also, although petrographic studies of shelf-type or "shelly" limestones are well-known (Beales, 1956; Cloud and Barnes, 1948), similar work on graptolite-bearing or "geosynclinal" limestones has never been published. Thus this is the first report of investigation of the latter limestones. To aid in the comprehension of the environments, the other rock types and the associated sedimentary features were also thoroughly treated. The limestone classification proposed by Folk (1957) (table 1) was found to be readily usable in this study; the writer agrees fully with the genetic concepts inherent in his treatment.

Rock samples were taken from every lithologic type of importance exposed in the Ordovician succession. The exact stratigraphic position of all of the rock types was determined and care was taken to include specimens from all parts of the region. A total of 75 samples was studied—60 of them in thin section. Acetate peels were made of the others. All of the dolomites and dolomitic limestones were subjected to staining with hematoxylin and etching by hydrochloric acid.

GENERAL COMMENTS ON THE ORDOVICIAN STRATIGRAPHY

A complete section of Ordovician rocks is exposed in the Marathon region. The better and more complete exposures are in the Marathon and Dagger Flat anticlinoria, which form the major part of the Marathon Uplift (fig. 1).

South and southeast from these uplifts in the Old Jones Ranch (now Slaughter Ranch), Persimmon Gap, and Rough Creek areas, Ordovician rocks occur at the surface in the crests of faulted anticlines. Small remnants of Ordovician strata are exposed along the front of the Sierra Santiago which is on the west and southwest sides of the Marathon uplift. Also, good exposures of

[1] Manuscript received May 26, 1958.

TABLE 1.—*A classification of limestones (after Folk, 1957, p. P-25)*

Limestones, Partially Dolomitized Limestones					
>10% Allochemical (Transported) Constituents Allochemical Rocks			<10% Allochemical (Transported) Constituents Microcrystalline Rocks		
Sparry calcite cement >Microcrystalline ooze matrix	Microcrystalline ooze matrix>Sparry calcite cement		1–10% Allochems		<1% Allochems
>25% Intraclasts	Intrasparrudite Intrasparite	Intramicrudite Intramicrite	Most Abundant Allochemical Constituent	Intraclasts: Intraclast-bearing Micrite	Micrite
<25% Intraclasts; >25% Oolites	Oosparrudite Oosparite	Oomicrudite Oomicrite		Oolites: Oolite-bearing Micrite	
<25% Intraclasts; <25% Oolites; Volume ratio of fossils to pellets 1:3	Biosparrudite Biosparite	Biomicrudite Biomicrite		Fossils: Fossiliferous micrite	
<25% Intraclasts; <25% Oolites; Volume ratio of fossils to pellets 3:1–1:3	Biopelsparite	Biopelmicrite		Pellets: Pelletiferous Micrite	
<25% Intraclasts; <25% Oolites; Volume ratio of fossils to pellets 1:3	Pelsparite	Pelmicrite			

Ordovician rocks are found in the Solitario, a small dome fifty miles to the south-southwest.

Although exposures are excellent, the Ordovician sequence was intensely folded and faulted so that complete stratigraphic sections of any formation are difficult to find. The exposures on the southeast limb of the Marathon anticlinorium are the least disturbed in the entire region.

The Ordovician section is composed of relatively thick beds of shale and thinner beds of dark limestone and chert. Intercalated with these beds are exotic boulders and lenses of conglomerate and sandstone. Graptolites, the most abundant fossils, may be found throughout the section. A few brachiopods, ostracods, trilobites, bryozoans, nautiloids, and sponges are also present. King (1931, 1937) mapped the Ordovician succession in the Marathon Basin and divided it into five formations. In ascending order the formations are: the Marathon Limestone, the Alsate Shale, the Fort Pena Formation, the Woods Hollow Shale, and the Maravillas Chert. The writer (in press) showed that the Alsate Shale is absent in the Solitario and Old Jones Ranch areas—its correlative being the Rodriquez Tank Sandstone. As indicated above, graptolites are plentiful throughout the section—occurring most commonly in the limestones. The author (in press and 1956) described the graptolite fauna, ascertained the ages of each of the formations, and recognized 15 zones based on graptolites. The Marathon Limestone is Early and earliest Middle Ordovician in age. The Alsate Shale, Rodriquez Tank Sandstone and Fort Pena Formations are all early Middle Ordovician in age, and the Woods Hollow Shale is mid-Middle Ordovician. The age of the Maravillas Chert is late Middle Ordovician and Late Ordovician.

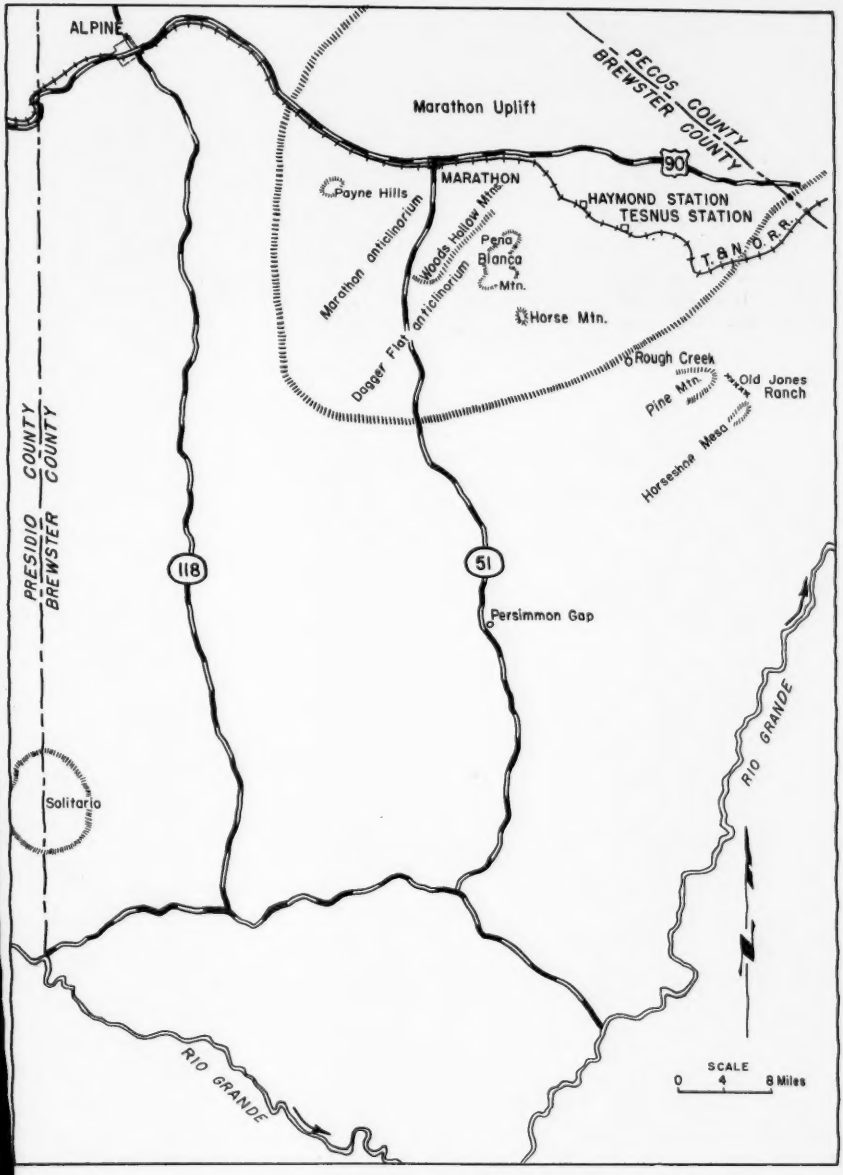

FIG. 1.—Index map of the Marathon region.

MARATHON LIMESTONE

General Features

The Marathon Limestone includes several limestone types, much black shale, many conglomerate lenses, and some lenses of subgraywacke, chert, and dolomite. The formation is divisible into three parts in the Marathon and Dagger Flat anticlinoria—the Monument Spring Dolomite Member and the beds above and below it.

The beds below the Monument Spring Dolomite Member range between 530 and 650 feet in thickness and are characterized by thick beds of black shale and many thinner beds of fine-grained, cross-laminated, dark gray limestone. Some beds of slabby, sublithographic, dark gray limestone that weather to a characteristic medium blue-gray color are also present. Interbedded with these three more common rock types are many lenses, of flat limestone slab conglomerate, and calcareous subgraywacke, and a few lenses of silty, pelletoid limestone, fine calcirudite, and orthoquartzite. The conglomerate lenses reach 10 to 15 inches in thickness and extend from a few feet to several yards along strike. The slabs within the conglomerate consist of thinly-laminated, cross-laminated, dark gray limestone and blue-gray weathering sublithographic limestone. They are elongate with maximum dimensions of 18 inches in length and 6 inches in width, and lie subparallel to one another in a matrix of coarse-grained subgraywacke. The subgraywacke lenses and the subgraywacke matrix of the conglomerate lenses are composed of small fragments of limestone, grains of quartz, plagioclase, glauconite, chert, and sericite with calcite cement. Many conglomerate lenses grade laterally into subgraywacke lenses. No graded bedding was observed in the subgraywackes.

Shale comprises about half of the lower part of the Marathon Limestone in the basin; in outcrops south of the basin the amount of shale increases greatly and subgraywacke lenses become thicker and more numerous. In Old Jones Ranch and Solitario exposures, shale beds and subgraywacke and orthoquartzite lenses make up nearly two-thirds of the thickness.

The Monument Spring Dolomite Member occurs about 550 to 650 feet above the base of the Marathon Limestone and ranges from 40 to 90 feet in thickness. It consists of oval lenses of fine-grained, gray dolomitic limestone aligned subparallel to each other and separated by shale and thin-bedded, cross-laminated, gray limestone. The weathered surface of the dolomitic limestone has a blue-gray and yellow mottled appearance. Where replacement by silica has occurred, it weathers a characteristic orange-brown. The individual lenses range in size from 10 feet long and 5 feet wide to 50 feet long and 25 feet wide. Fossil fragments are common in them; there are vague algal structures, sponges of the type of *Archeoscyphia*, orthoid brachiopods, and cephalopods. The oval masses that characterize the Monument Spring Member were probably patch reefs constructed principally of algae and sponges. The member thins southward across the Marathon Basin and is not present in the Solitario and Old Jones Ranch areas.

The beds above the Monument Spring Dolomite Member are about 250 feet thick and consist of dark-gray, blue-gray weathering, sublithographic limestone in beds 4 to 8 inches thick interbedded with thinly-laminated cross-laminated, dark-gray, fine-grained limestone in beds 4 to 6 inches thick. Beds of black shale, buff argillaceous limestone, and lenses of flat-limestone-slab conglomerate, and subgraywacke are subordinate rock types. To the south, in the Old Jones Ranch and Solitario exposures, the upper part of the Marathon Limestone includes several beds of brown-weathering, arenaceous limestone, beds of orthoquartzite, and more shale beds than in the Marathon Basin.

Several kinds of sedimentary features are present throughout the Marathon Limestone. The thin, buff, argillaceous limestone layers found sporadically throughout the upper part of the formation bear well-developed mud cracks. The weathered surfaces of some of the limestone beds are thickly strewn with siliceous sponge spicules, whereas other limestone bedding surfaces bear minute channel markings and are overlain by one-eighth to one-quarter inch layers of sandstone. Commonly such sandstone layers are crowded with worn, broken valves of inarticulate brachiopods. Still other limestones are penetrated by small tubes filled with comminuted material, per

haps left by a burrowing animal. A prominent feature of many of the limestone layers is the cross-lamination. A study of the direction of dip of the cross-laminae in these beds indicates that the last current to pass over them came from the southwest.

Microscopic Study

Study of thin sections of the limestones which are included in the Marathon Limestone reveals that the dominant type is a micrite (plate 1, fig. 1). Most of the blue-gray-weathering, sublithographic limestone is a pure micrite, but some of it is a pelletoid micrite or pelmicrite. The pellets are well-rounded, fairly well-sorted, and fall within a size range of .04 to .12 mm in diameter. Commonly, in this pelmicrite, finely crystalline (.01 to .05 mm in maximum dimension) sparry calcite encloses small areas of micrite. The patchy distribution of the sparry cement, and the fact that bits of micrite are enclosed by sparry grains, suggests that the sparry material is recrystallized micrite. Most of these pelmicrites are minutely laminated. Figure 2 on plate 1 shows the pellets surrounded by micrite and some recrystallized micrite.

The thinly-laminated, commonly cross-laminated, dark-gray limestone is also a pelmicrite. These pelmicrites commonly have minute laminae of pelsparite interlaminated with the pelmicrite. Some of the sparry cement does not appear to be recrystallized micrite but much of it is. Commonly, during weathering the pelsparite or pelmicrosparite laminae have gone into solution faster than the pelmicrite laminae, and as a result the cross-laminae are quite conspicuous on the exposed surface.

These kinds of limestones constitute more than 90 percent of that rock type in the Marathon Formation. Scattered throughout them are siliceous sponge spicules, a few calcispheres .04 to .06 mm in diameter, and very fine subangular sand size grains of quartz. Because their size is out of proportion to that of the enclosing lime mud, it is supposed that the quartz grains were probably blown into the depositional site. Commonly, these limestones have been partially dolomitized—up to approximately 10 percent.

Other limestone types are uncommon in the Marathon Limestone and are nearly all restricted to the lower part of the formation. One type, in which trilobites and molluscs were found, is composed of fossiliferous biomicrite pebbles in a sparry, calcitic matrix. Included in the pebbles are fragments of trilobites, spired gastropods, ostracods, brachiopods, echinodermal plates, sponge spicules, and algae. The sparry cement is very coarsely crystalline (1 to 3 mm in maximum dimension), and small stringers of chert are found in it.

Another limestone type present in the lower part of the formation is a silty pelmicrite. In it many subangular, coarse silt-sized quartz grains, some chert, and a few plagioclase grains are scattered throughout pelletoid micrite.

The pellets in the Marathon Limestone are probably faecal pellets—the product of burrowing organisms, possibly worms, which tunnelled through and ingested lime muds. Some of the micrites contain bits of brown phosphatic material.

Dolomite and dolomitized limestones comprise the Monument Spring Dolomite Member. The fossil fauna of the member is different from that of the other parts of the Marathon Limestone. It includes cup-shaped sponges, algae, orthoid brachiopods, nautiloids, and gastropods. Blocks of the member were etched in hot hydrochloric acid and the resultant texture was studied. The dolomitic limestone portions dissolved, leaving vugs and pockets in the undissolved portions of the blocks. A block that was so treated is illustrated on plate 2. The dolomite may well have been formed where highly magnesian algae once grew. The algae formed traps for the bioclastic debris, the material which is now only partially dolomitized. Thin section study of the dolomitic limestone shows it to be a lime mud or micrite with many fossil fragments scattered throughout. It is a partly dolomitized biomicrite. The dolomite portion is finely cyrstalline and a few fossil fragments are scattered in it.

The oval lenses of dolomite and dolomitized limestone that characterize the Monument Spring Member were doubtless once small reef masses built up primarily of algae which acted as trappers and binders of organic fragments. The reef masses probably resembled, in size and possibly in shape, small patch reefs found in the lagoons of

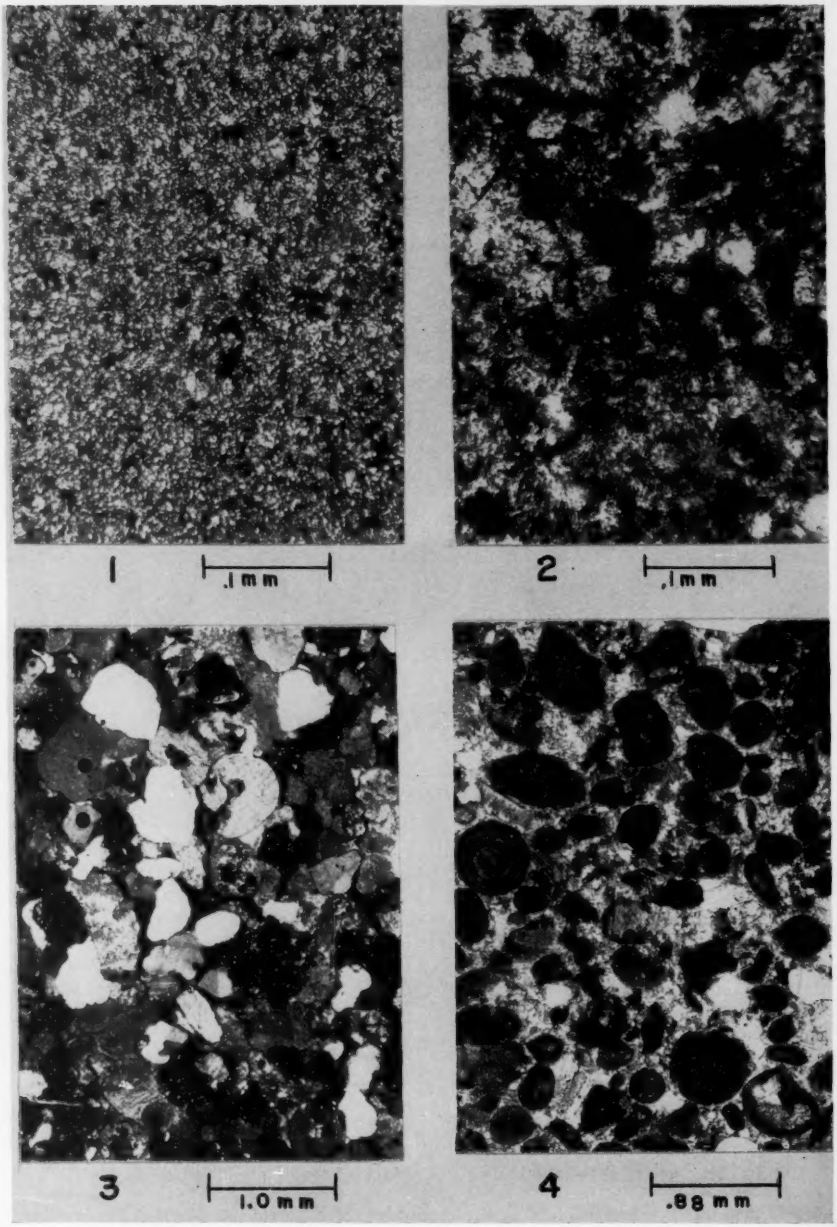

PLATE 1

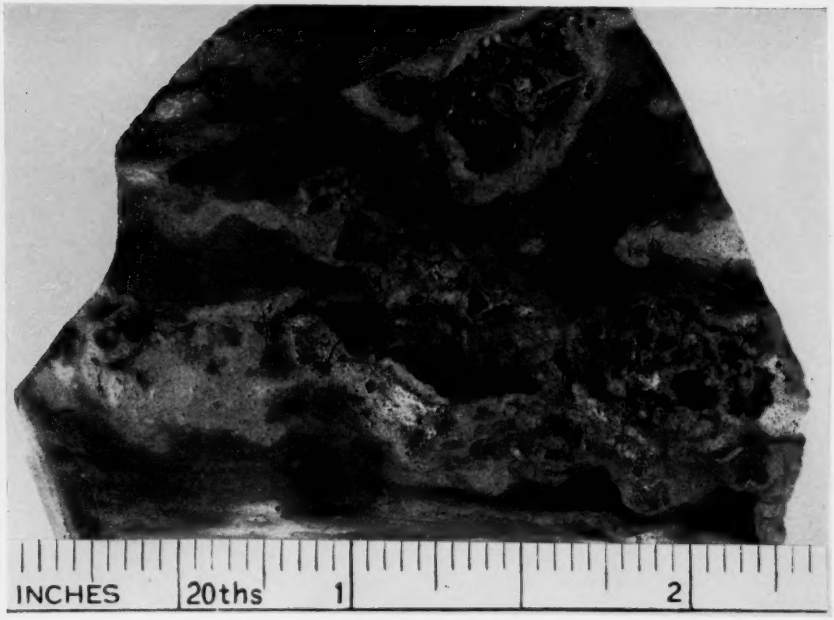

PLATE 2

A block of Monument Springs Dolomite that has been etched in hydrochloric acid. The dark gray laminated areas are algal remains—now dolomites; the light gray areas are limestone and dolomitic limestone; and the darkest patches in the center of the light portions are silicified bioclastic debris.

modern coral atolls.

In addition to the limestones and shale, subgraywacke and flat-limestone-slab conglomerate lenses are conspicuous rock types in the Marathon Limestone. The conglomerates are composed of slabs of the typical micrites and pelmicrites which characterize the formation; lying in subparallel alignment in a matrix of small pebbles of micrite, pelmicrite, and silty micrite, and of subangular grains of plagioclase, chert, and quartz. The conglomerates are of small lateral extent and some grade into pelmicrite or silty pelmicrite, whereas others grade into subgraywacke. The manner in which the slabs and pebbles formed is open to conjecture. Richter (1924, p. 163–164) reported flat pebbles accumulating in deep water, and van Straaten (1954, p. 38) found features indistinguishable from mud cracks beneath a cover of water. Thus the formation and accumulation of flat pebbles subaqueously may be possible; however, it is doubtful that pebbles formed in such a manner would be of firmly cohesive material several inches thick. The most commonly accepted concept

EXPLANATION OF PLATE 1.

FIG. 1.—Marathon Limestone. Micrite.

FIG. 2.—Marathon Limestone. Pelmicrite. The larger black objects are pellets and the larger white grains are quartz. Micrite surrounds the pellets, and the larger light areas are grains that commenced aggredational recrystallization.

FIG. 3.—Marathon Limestone. Subgraywacke. Bits of micrite comprise most of this rock.

FIG. 4.—Fort Pena Formation. Oölitic intrasparite. The oölites and intraclasts are cemented by medium crystalline sparry calcite cement.

of the origin of flat pebbles is that they formed as polygons between mud cracks during subaerial desiccation. The slabs and chips composing the conglomerates in the Marathon Limestone probably were formed in this manner when local sectors of the bottom were exposed. Then storm-generated waves or currents swept over the area, scoured the bottom, ripped up slabs and pebbles of partially consolidated limestone, and with very little net transport of the larger slabs dropped them back to the bottom. The quartz and plagioclase grains were possibly derived from some nearby source land which was eroded during the storm, the beach material going into suspension, and then (because of the decrease in competence of the transporting medium) being deposited with the limestone pieces.

Subgraywacke lenses are numerous in the lower part of the Marathon limestone and are rare in the upper part. They are composed (plate 1, fig. 3) of subangular grains of quartz and plagioclase, glauconite and sericite grains, chert and limestone oölites, and many fragments of micrite and pelmicrite. Rock fragments are the most abundant components, comprising the major part of the rock. Quartz makes up 5 to 14 percent and plagioclase about 1 percent. A small amount (5 percent or less) of fine-grained calcitic matrix is present, but calcite cement fills most of the interstices. The subgraywacke lenses are poorly sorted and none displays graded bedding. They probably originated in the same manner as did the conglomerates except that the currents were not strong enough to take up anything larger than coarse sand sized grains from the bottom. Possibly the increased quartz content made the currents less competent.

Calcareous, fine-grained quartz sandstone is another rock type found in a few places in the Marathon Limestone. The quartz grains are subangular. A few plagioclase grains and occasional glauconite grains are present in this sandstone.

Another rock type—this one found only in the lower part of the formation—is present. This type is a quartz rudite composed of two sizes of angular quartz grains. Most of the grains are about .4 mm in maximum dimension, whereas other grains are 1 to 5 mm in maximum dimension. The grains are bound together by sparry calcite cement.

A study of the quartz grains from all parts of the formation indicates two different origins for them. Most of the grains have straight extinction, contain no inclusions, and probably are of plutonic formation. The other quartz grains have undulose extinction and are made up of smaller individuals with sutured or crenulate boundaries between them. These latter grains came from a metamorphic rock—possibly a gneiss. The presence of grains of sodic plagioclase in many parts of the formation adds credence to the postulation of a gneissic source for some of the quartz grains.

Environment of Deposition

From a consideration of the internal and external features displayed by the rocks grouped within the Marathon Limestone, a general picture of the environment may be obtained. The region was one of accumulation of mud—for a part of the time lime mud—and for nearly a similar length of time, clays. Predominantly clay deposition with varying admixtures of lime mud and quartz sand took place in the southern part of the Marathon region (Solitario and Old Jones Ranch areas) during nearly all of the time of deposition of the Marathon Limestone. In the northern part of the region (Marathon Basin), similar deposition took place during earliest Ordovician time. Then lime mud became the dominant material in the northern part of the region, and deposition of it progressively increased in proportion to the clastic materials throughout the time of deposition of the formation. Burrowing organisms tunnelled through large areas of this region of mud accumulation, and from time to time currents from the southwest passed over the region and rolled faecal pellets into cross-laminae. Commonly local sectors of the bottom were exposed, dried, and desiccation cracks were formed leaving large polygons. After a relatively short period of exposure waves, perhaps storm generated waves, swept over these sectors, ripped up pebbles and slabs, and then dropped them back to the sea floor.

The waters were undoubtedly kept turbid by frequent wave agitation; therefore organisms could dwell only in the surface layers. Thus, remains of pelagic organisms, graptolites and minute calcareous protistids, are the only forms of life found in the rocks. For

a short period during the middle part of the Early Ordovician time, the waters must not have been so turbid because algae grew, trapped sediment, and small reef mounds formed. The larvae of other benthonic organisms were attracted to the reefy area and flourished there. Later, wave action increased, the waters became more turbid, and sediment washed around and over the reefs, ending their development.

ALSATE SHALE AND RODRIQUEZ TANK SANDSTONE

After deposition of the micrites in the Marathon Basin, a period of clastic deposition ensued. The water over the bottom remained stable, a reducing condition developed, and the black muds, now comprising the Alsate Shale, accumulated. To the south, in the Old Jones Ranch and Solitario areas, an orthoquartzite was deposited at the same time that the Alsate Shale was laid down in the Marathon basin. The Rodriquez Tank Sandstone is composed of well-rounded, fairly well-sorted, fine-grained sand size quartz particles. Overgrowths formed on some of the quartz grains. Extremely fine-grained chert is the cementing substance. The quartz appears to have been derived from a pre-existing sedimentary rock, although ultimately it probably originated in a plutonic rock.

Faunal evidence indicates that the Alsate Shale and the Rodriquez Tank Sandstone were deposited in a comparatively short time. Then carbonate deposition again began in the Marathon region.

FORT PENA FORMATION

General Features

The Fort Pena formation consists of purple chert in layers 2 to 6 inches thick, alternating with black shale in layers 4 to 24 inches thick, brown-weathering, thinly-laminated, commonly cross-laminated, gray limestone in layers 4 to 18 inches thick, calcareous subgraywacke in layers 4 to 17 inches thick, and limestone and chert pebble conglomerate in layers 3 to 10 inches thick. There is no rhythm to the alternations of rock types; one type extends for several yards along strike and then passes into another.

The lithic character of the Fort Pena Formation is remarkably uniform over its entire outcrop in the Marathon basin. In the Old Jones Ranch and Solitario areas it includes thicker and more numerous shale and sandstone beds.

The dip of the current laminae indicates that the last current to pass over the cross-laminated limestone layers came from the southwest. Also several beds with biserial graptolites arranged with their long axes subparallel were found near the top of the formation. The proximal (narrow) ends of the rhabdosomes point S25W to S40W, indicating that the last current to pass over these rhabdosomes came from the southwest.

Microscopic Character

The majority of the limestones in the formation appear to be intrasparites (plate 1, fig. 4). Many of the particles composing the rock are pieces of penecontemporaneous, weakly consolidated calcium carbonate sediments that were torn up and redeposited by strong currents; hence they are true intraclasts. Some of the particles, however, appear to have been formed by aggregation of minute calcium carbonate grains and are therefore pseudo-intraclasts according to Folk (1957). A better term for them might be lumps because they are like the lumps described by Illing (1954, p. 29–30). The intraclasts and lumps are well-rounded and well-sorted, the majority of them falling within a size range of .15 to .23 mm in maximum dimension. Many of the supposed intraclasts may actually be lumps in which the once-discrete grain aggregates have become highly compacted and so now appear to be intraclasts. A few of the intraclasts and lumps have been bored by algae (plate 3, fig. 2).

Most of the other limestones in the formation are oösparites or oölitic intrasparites. All of the intrasparites have a few oölites in them and all gradations are present between intrasparites with a few oölites and oösparites with a few intraclasts. The oölites are identical in structure to those on the Bahama Banks described by Illing (1954, p. 35–41). They are composed of two parts, an inner zone or nucleus and an outer zone of concentric layers. The nuclei commonly are sharply defined, but they may merge with the innermost concentric layer. They are composed of minute grains of calcium carbonate and are structureless. The outer con-

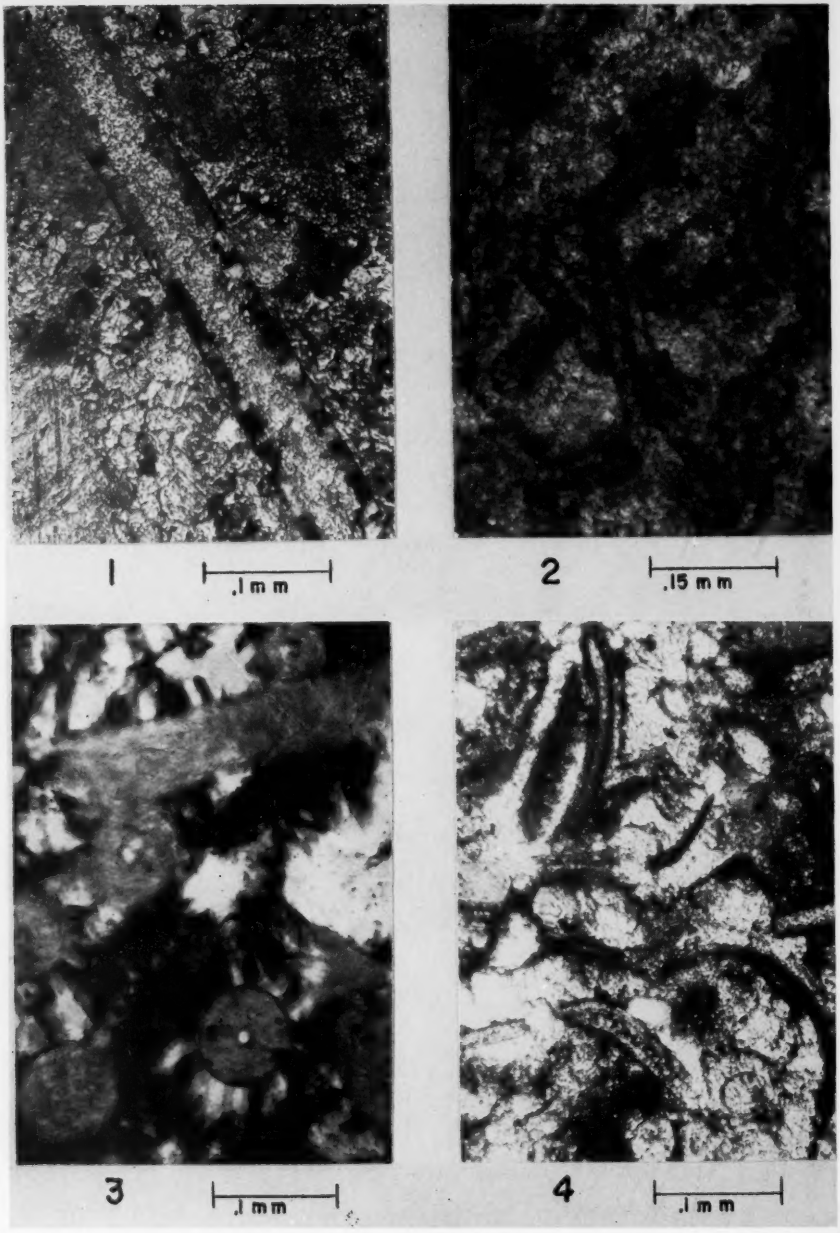

PLATE 3

FIG. 1.—Fort Pena Formation. Cross-section of a sponge spicule that is part chert and part calcite.
FIG. 2.—Fort Pena Formation. Algal borings in an intraclast.
FIG. 3.—Fort Pena Formation. Sponge spicules, now calcite, in chert.
FIG. 4.—Woods Hollow Shale. Ostracod valves cemented by finely crystalline calcite cement.

centric layers commonly display a faint radial structure. The oösparites, like the intrasparites, are well-sorted. Most of them fall within a size range of .35 to .55 mm in diameter. The cementing material of the intrasparite-oösparite group is medium to coarsely crystalline (.1 to 1 mm in maximum dimension) calcite.

Sponge spicules, subangular fine sand-size quartz grains, ostracod and brachiopod valve fragments, chert oölites, and a few dolomite, glauconite, and plagioclase grains are scattered throughout the cement of the intrasparite-oösparite clan. In some places, sponge spicules comprise 2 to 3 percent of the rock. All of the spicules have a central canal, as do all modern siliceous spicules (Cayeux, 1931, p. 391). Some of these spicules are now chert, some are part chert and part calcite (plate 3, fig. 1); but most are now composed of calcite.

Another carbonate type, forming a minor part of the limestone in the formation, is a microsparite. This type is a micrite that has recrystallized so that now the individual grains are very finely crystalline calcite and are larger than those of micrite. Angular, fine sand-size quartz grains and sponge spicules are scattered throughout the microsparites. This limestone type passes literally into oölitic intrasparite and all gradations between the two kinds are present.

The chert in the formation is thinly-laminated and is composed of a mat of radiating chalcedony fibers. Scattered through the chert are subangular, fine sand-size quartz grains, calcite grains, faecal pellets of reworked calcareous siltstone, phosphatic bits, fragments, and hollow spicules, most of which are now calcite (plate 3, fig. 3).

This chert was probably formed by replacement of certain limestone beds, especially those in which a high concentration of siliceous sponge spicules could locally supply relatively large amounts of silica. Because phosphatic fragments and faecal pellets are conspicuous, these limestone beds may also have been ones in which an acidic environment was formed by the decomposition of relatively large amounts of organic matter. If so, a hypothesis suggested by Fisher (in Newell and others, 1953, p. 163–166) for the origin of chert in the Delaware Basin may be invoked. The hypothesis follows from the influence of pH on the solubility of silica and calcium carbonate in water. Correns (1950) showed these are diametrically opposed, so that decrease in pH results in depression of the saturation point of silica and a corresponding elevation of the saturation point of calcium carbonate. During diagenesis, as a consequence of pH differences in the limestone beds, silica would be dissolved from the siliceous spicules outside an acidic environment and precipitated within it, while calcite would be dissolved within an acidic environment and precipitated outside of it.

The subgraywacke and conglomerate lenses in the formation are composed of chips of shale and limestone and many smaller intraclasts; these are set in a matrix of microsparite (recrystallized micrite). Subangular, fine sand-size grains of quartz and feldspar, glauconite grains, and valve fragments of ostracods and brachiopods are scattered through the matrix. These rocks probably originated during storm periods when wave action was strong enough to rip up pieces of more strongly consolidated sediment as well as weakly aggregated material.

The quartz grains present in all parts of the formation had either a metamorphic origin or an igneous one. About half of the grains appear to have come from a metamorphic source; the other half had a plutonic origin. The plagioclase grains are highly sodic and also apparently were derived from a metamorphic rock.

Environment of Deposition

Carbonates were the dominant sediment accumulated during the time of deposition of the Fort Pena Formation. The bottom was obviously subjected to strong current action which ripped up pieces of weakly consolidated material and at times more firmly consolidated material, rolled them about, sorted and rounded the fragments, and winnowed out the fines. Oölites were also formed in the region, probably under conditions similar to those described by Illing (1954, p. 43–44) for modern ones on the Bahama Banks. From the evidence provided by the dip of the current laminae and the alignment of the biserial graptolites, the last currents to sweep the region came from the southwest.

During short periods of relative quiescence clays and micrite were deposited. They ac-

cumulated in local areas only, possibly areas over which the water column became stable because of a temporary density stratification.

Thus the depositional site was an area where warm marine waters saturated with calcium carbonate were washed back and forth over a shallow sea floor. Only in local areas and for short periods of time was the almost continual current agitation inhibited.

WOODS HOLLOW SHALE

General Features

The formation consists of greenish-weathering, black shale with interbedded layers of gray, thinly-laminated limestone and tan-weathering calcareous siltstone, each $\frac{1}{4}$ to 1 inch thick, and lenses of yellow-brown weathering conglomerate composed of flattened pebbles of black shale scattered in a gray limestone matrix. The thin beds of limestone and siltstone are more numerous in the basal 60 to 80 feet of the formation. Some of the shale beds bear mud cracks and some of the siltstone and limestone beds display current ripple marks.

The contact of the Woods Hollow Shale and the Fort Pena Formation is gradational. Where seen, the top 10 feet of the Fort Pena Formation is a thin-bedded, brown-weathering, gray limestone in layers a few inches thick with interbedded black shale. The basal 20 feet of the Woods Hollow Shale includes thin-bedded, tan-weathering, gray limestone in layers up to 2 inches thick and gray shale pebble conglomerate lenses, both interbedded with greenish-weathering black shale.

Locally, the upper beds of the formation contain more layers of thinly-laminated gray limestone interbedded with the black shale. Aside from these minor differences, the Woods Hollow Shale is remarkably uniform in lithology, and apparently in thickness, throughout the entire Marathon region.

At a few localities, principally in the southwestern part of the Marathon Basin, the upper 50 to 100 feet of the formation contains scattered, rounded boulders of Early Ordovician and Late Cambrian limestone. Wilson (1954) made a detailed study of the boulders and their faunas and showed that the boulders contain trilobites belonging to the Atlantic as well as the North American faunal realm. In his opinion, the boulders slumped off a Middle Ordovician fault scarp and were emplaced in the mud of the Woods Hollow Shale by violent storms.

Graptolites are commonly aligned on the limestone and siltstone bedding surfaces and the proximal (narrow) ends of their rhabdosomes point to the southwest, thus indicating that the last current to pass over them came from that direction.

Microscopic Character

The limestone grains are predominantly ostracod valves. In one kind—biosparite—the valves lie at all angles to the bedding and are cemented by sparry calcite which is .05 to .12 mm in maximum dimension. In another type, biomicrite (plate 3, fig. 4), the valves lie with their long axes parallel in a matrix of micrite or recrystallized micrite. The micrite matrix bears faecal pellets, which are well-rounded and fall within a size range of .03 to .06 mm in diameter, and many brown phosphatic shreds. Phosphatic fragments are also present in the biosparites. Some of the biosparite layers grade up into biomicrite. Angular, silt-sized quartz grains and a few siliceous sponge spicules are scattered through both the biomicrites and biosparites.

The siltstones (plate 4, figs. 2, 3) are thinly-laminated and are composed of well-sorted, angular, coarse, silt-sized, quartz grains. Sparry calcite is the cement. In places abraded ostracod valves, lying with their lengths and widths parallel with the lamination, form minute layers. Some glauconite grains and bits of phosphatic material are also present.

The conglomerate lenses are composed of flattened pebbles of black shale in a matrix of micrite. Angular, silt-sized quartz grains and abraded ostracod valve fragments are scattered through the matrix and some sparry calcite cement is present.

The quartz grains are all approximately the same size and nearly all of them had a plutonic provenance. A few of the grains came from a metamorphic rock; they exhibit undulose extinction and crenulate boundaries.

Environment of Deposition

A gradual change in rock types is present between the thin, thinly-laminated lime-

stones and shales at the top of the Fort Pena Formation and the predominant shale and some thin limestone at the base of the Woods Hollow Shale. This transition reflects the slow change between the environments in which the two formations were deposited.

Clays accumulated and black muds were formed in the Marathon region during the time of deposition of the Woods Hollow Shale. Some of the shale layers bear mud cracks and their presence indicates that for short periods of time parts of the area were temporarily exposed.

Only a few remains of pelagic organisms, graptolites, were found in the shales, but graptolites are common in the limestones and siltstones. Also, the limestones are composed largely of ostracod carapaces many of which are abraded.

Thus the region may have been a broad mud flat across which tides fluctuated and parts of which, temporarily at least, were exposed. Currents carrying ostracod and graptolite skeletal remains, some quartz grains, and a few sponge spicules periodically swept across this low area. At times, the quartz component of the transported load was greater than the skeletal component, and at other times the currents were strong enough to rip up small pebbles of shale from the bottom. Commonly, after the ostracod valves were dumped, a shallow sheet of water remained over the region or parts of it. While it was present, lime muds accumulated and burrowing organisms tunnelled through them. After short intervals of carbonate deposition clays once again accumulated. The aligned graptolites indicate that the lime, graptolite, ostracod-bearing currents came from the southwest.

The exotic boulders occur in a local area on the southwest side of the Marathon Basin in the upper part of the formation. They are isolate masses surrounded by intensely contorted shale and probably slid or rolled off a rising scarp—possibly to the west.

MARAVILLAS CHERT

General Features

The formation is composed of layers of black chert 6 to 8 inches thick alternating with light gray weathering, black, petroliferous limestone layers 4 to 8 inches thick. Also, it includes some interbedded lenses of black chert and limestone pebble conglomerate, a few thin, pink weathering shale partings, and a few layers of subgraywacke 4 to 6 inches thick, some of which exhibit graded bedding. Both the black chert and the limestone are lenticular and intergrade along strike. Near the middle part of the formation on the southeast flank of the Dagger Flat anticlinorium several beds of coarse-grained calcarenite 2 to 10 feet thick occur. These beds contain abundant fragments of bryozoa and trilobites. A conglomerate up to 10 feet thick is present in a few places at the base of the formation. Black chert and limestone slabs are common in the conglomerate. It also includes rock types not found in the Marathon region, such as a brownish, medium-grained, quartzose sandstone and a pinkish dolomite. The conglomerates are merely lenses and pass into beds of black chert or limestone along strike. South of the basin in the Solitario, Persimmon Gap, Rough Creek, and Old Jones Ranch exposures, chert predominates over limestone.

Microscopic Character

Carbonates comprise between 40 and 45% of the Maravillas Chert, and they are almost evenly divided between limestones and dolomites. The limestones are all of one type, micrite (plate 4, fig 1). They are all minutely laminated and nearly all have been slightly dolomitized. The dolomites (plate 4, figs. 4, 5) are composed of 70 to 80% finely crystalline (.02–.04 mm in diameter) rhombs and nearly all of the remainder of the rock is micrite. Patches of micrite are surrounded by dolomite rhombs and the rhombs project in to the micrite; therefore the micrite probably has been replaced by dolomite. These calcitic dolomites have a greater porosity than the limestones and they emit a strong petroliferous odor when struck.

Scattered through the micrites and calcitic dolomites are sponge spicules, angular, silt-size grains of quartz, calcispheres .04 to .06 mm in diameter, a few radiolaria, and abraded ostracod valve fragments. Sponge spicules are locally abundant, forming 1 to 2 percent of the rock. Dark brown phosphatic shreds and graptolites are locally prominent in these rocks and in all the rocks the mi-

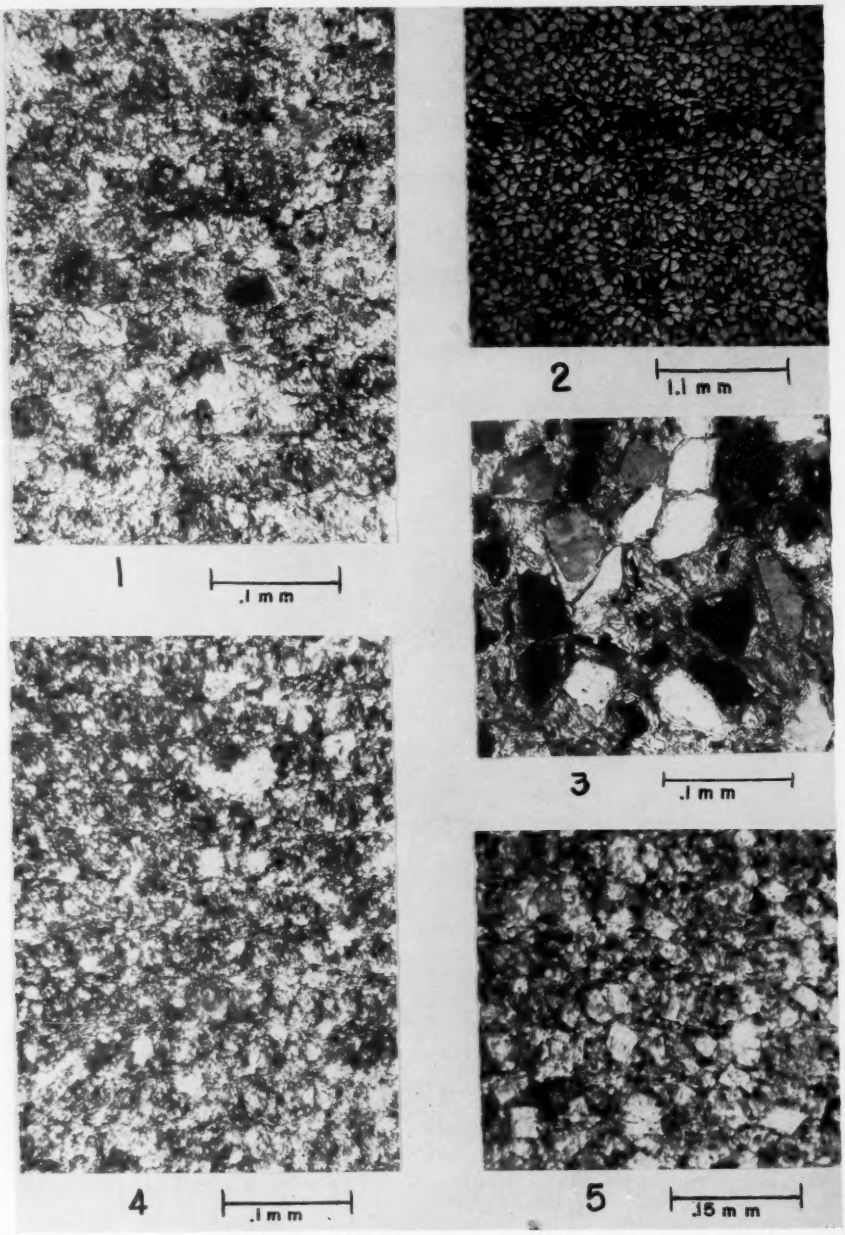

PLATE 4

crite is heavily stained with a brown substance, possibly petroleum.

The calcirudite beds, common in the middle part of the formation on the southeast limb of the Dagger Flat anticlinorium, are biosparrudites. They are composed of numerous fragments of bryozoa and trilobites and contain some fragments of brachiopods and ostracods. The fragments are cemented by a very coarsely crystalline calcite which is 1 to 4 mm in maximum grain dimension. These beds probably represent local areas of the sea floor where bryozoa flourished and to which other organisms were attracted by the abundance of food.

The cherts in the formation are finely-laminated and are composed of a fine-textured mass of cryptocrystalline quartz. Scattered through the chert are many sponge spicules, some angular silt-sized grains of quartz, small bits of dolomite and dolomitic siltstone that show alteration rims and probably passed through the gut of an animal, graptolites, spore-like entities, calcispheres, phosphatic shreds, a few radiolaria, and a small amount of finely divided pyrite. Locally small calcite grains and fragments of bryozoa and brachiopods occur in the chert. Spicules are abundant in places —forming 3 to 4 percent of the rock. This chert, like that of the Fort Pena Formation, appears to have replaced beds of limestone. The chert layers grade laterally and vertically into micrite; however, organic remains are more prominent in the chert. Thus the present chert beds may have been those of micrite in which chertification took place during diagenesis because of pH differences.

The lenses of subgraywacke and conglomerate are composed of subangular pebbles of penecontemporaneous, black chert and micrite in a matrix of calcite. Some of the interstices are filled with calcite cement. Angular, coarse, silt-sized particles of quartz, plagioclase, and glauconite are scattered in the matrix. The size of the pebbles ranges from coarse sand to medium rudite and the subgraywackes commonly grade either laterally or vertically into conglomerate. The pebbles probably formed when areas of the bottom dried out and cracks formed. Subsequent rush of strong current action—possibly storm generated—ripped up pebbles and smaller particles, carried them a short distance, and then redeposited them. The presence of black chert occurring as pebbles indicates that chertification of the limestone took place almost immediately after deposition—during the earlier phases of lithification. The exotic slabs which occur in the local conglomerate lenses at the base of the formation are found only 15 feet stratigraphically higher than the highest of those in the Woods Hollow Shale in the same part of the basin. Therefore, they may have come from the same or a similar fault scarp—rolling and sliding to their present position.

The quartz grains in the Maravillas Chert, like those in the lower part of the Ordovician succession in the Marathon region, had two different origins. The majority of the grains had a plutonic provenance, but a few display sutured edges and undulose extinction and are therefore considered to be of metamorphic derivation. The few plagioclase grains in the formation are highly sodic in composition and they, too, are probably from a metamorphic source.

Environment of Deposition

The sediments that now comprise the Maravillas Chert were deposited very slowly over a long period of time (late Middle Ordovician to the end of the Ordovician), as indicated by the fauna. For most of the time, the region was one of lime-mud

EXPLANATION OF PLATE 4

FIG. 1.—Maravillas Chert. Micrite with a few dolomite rhombs.

FIG. 2.—Woods Hollow Shale. Siltstone composed of angular quartz grains cemented by crystalline calcite. The black shreds lying parallel to the bedding are graptolite bits.

FIG. 3.—Woods Hollow Shale. Part of figure 2 enlarged, showing grain borders of the quartz grains partly corroded by calcite.

FIG. 4.—Maravillas Chert. Micrite and some dolomite rhombs. This is an intermediate step in a recrystallization sequence of limestone to dolomite which starts with micrite and a little dolomite (fig. 1) and ends with mostly dolomite and some micrite (fig. 5).

FIG. 5.—Maravillas Chert. Dolomite with some micrite. This rock is near the end stage of the recrystallization sequence.

accumulation under reducing conditions. Locally, for brief periods, clay was deposited instead of lime. Also, some areas of the bottom were subjected to drying and cracking from time to time. Several such areas existed during the earliest part of the time of accumulation of the Maravillas Chert, and they probably indicate a slow transition of environment from a mud flat of clay deposition to a nearly permanently subaqueous area in which lime mud was accumulating.

In a local area on the south central side of the Marathon Basin, bryozoa flourished and built small biostromal mounds to which trilobites and a few ostracods and brachiopods were attracted. These mounds were built up over small areas of the bottom that were free from toxic waters for a time, but then when the foul waters returned, bryozoan growth ended. This process recurred several times in small sectors during part of the Late Ordovician.

Thus the site of deposition was an area covered by calm, probably warm, marine waters in which a reducing environment developed. Only locally and for relatively short periods of time was the water mass disturbed or the toxic condition of it diminished.

CONCLUSIONS

The Ordovician succession in the Marathon region is in general an accumulation of muds—dominantly calcareous in composition. The muds were deposited in a variety of environments, ranging from the agitated, turbid waters of the Early Ordovician to the shallow-bottom, strong-current action of early Middle Ordovician to the mud flat in the latter part of the Middle Ordovician to the calm, stable water of the Late Ordovician.

Most of the fossils found in the rocks are the remains of pelagic organisms—graptolites primarily. The graptolites occur principally in the limestones and are present in those limestones formed under strong current action as well as those formed under weak current activity. Most of the better specimens were found in low relief on the bedding planes of those limestones formed under the strongest current action, the oölitic intrasparites, but many good specimens were found preserved as black films on the gray micrites of the Marathon Limestone.

The preponderance of evidence points to shallow water prevailing over the region throughout the entire Ordovician. Reef masses and biostromal beds are included in the Marathon Limestone and the Maravillas Chert respectively. The shales of the Woods Hollow Shale and some of those in the Marathon Limestone bear mud cracks. Further, the cross-laminated limestones of the Fort Pena Formation are composed of oölites, intraclasts, and aggregates, indicative of a sea floor shallow enough to be agitated by wave action.

Aligned biserial graptolite rhabdosomes in the Fort Pena and Woods Hollow Formations and the direction of dip of the cross-laminae in the Marathon and Fort Pena Formations clearly indicate that the last current to pass over the area during the time of deposition of these formations came from the southwest. Little current activity took place during the time of deposition of the Maravillas Chert.

The nature of the quartz grains scattered throughout the Ordovician succession indicates diverse derivations for them. Most of the grains had a plutonic origin whereas some had a metamorphic provenance. The quartz grains forming the Rodriquez Tank Sandstone are at least second-cycle sedimentary quartz, ultimately derived from a plutonic rock.

The bedded cherts in the sequence are postulated to be replaced limestones. In certain limestone layers, because of pH differences between them and the surrounding limestone, chertification took place. No nearby land mass was sufficiently weathered to supply pure silica to the sea water for deposition in the colloidal state, and no nearby volcanic activity is known.

Thus, during Ordovician time, the Marathon region was the site of shallow water deposition of calcareous mud micrite and clay with some pelsparite, intrasparite, and biosparite admixed. The waters were agitated and turbid, and the bottom was frequently disturbed in the Early Ordovician and early part of the Middle Ordovician. Then a tidal mud flat environment became dominant. Currents swept across the flat periodically, bearing in them remains of pelagic organisms. Abruptly, in the latter part of Middle Ordovician time, waters of shallow depth

returned to the region. These waters were but little affected by waves or currents and a reducing condition was present in them—above the water-sediment interface. This environment persisted in the Marathon region until the end of the Ordovician.

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REFERENCES

Beales, F. W., 1956. Conditions of deposition of Palliser (Devonian) Limestone of southwestern Alberta: Am. Assoc. Petroleum Geologists Bull., v. 40, p. 848–870.

Berry, W. B. N., 1956, Graptolites from the Marathon region, west Texas (abs.): Geol. Soc. America Bull., v. 67, p. 1670–1671.

———, (in press), Graptolite faunas of the Marathon region, west Texas: Univ. Texas Bull.

Cayeux, M. L., 1931, Introduction a l'etude petrographique des roches sedimentaires: Imprimerie Nationale, Paris. 774 p.

Cloud, P. E., Jr. and Barnes, V. E., 1948, The Ellenburger Group of central Texas: Texas Univ. Bull. 4621. 473 p.

Correns, C. W., 1950, Zur geochemie der diagenese: Geochimica et Cosmochimica Acta, v. 1, p. 49–54.

Folk, R. L., 1957, Petrology of sedimentary rocks. Hemphill's, Austin, Texas.

Illing, L. V., 1954, Bahaman calcareous sands: Am. Assoc. Petroleum Geologists Bull., v. 38, p. 1–95.

King, P. B., 1931, Pre-Carboniferous stratigraphy of Marathon uplift, west Texas: Am. Assoc. Petroleum Geologists Bull., v. 15, p. 1059–1085.

———, 1937, Geology of the Marathon region, Texas: U. S. Geol. Survey Prof. Paper 187. 148 p.

Newell, N. D., Rigby, J. K., Fischer, A. G. Whiteman, A. I., Hickox, J. E., and Bradley, J. S., 1953, The Permian reef complex of the Guadalupe Mountains region, Texas and New Mexico: W. H. Freeman and Company, San Francisco, 236 p.

Richter, R., 1924, Schlickgerolle auf dem Meeresgrund entstehend: Senckenbergiana, v. 6, p. 163–164.

Straaten, L. M. J. U. van, 1954, Sedimentology of Recent tidal flat deposits and the Psammites du Condroz (Devonian): Geol. en Mijnb. (Nw. Serie), jg. 16, p. 25–47.

Wilson, J. L., 1954, Late Cambrian and Early Ordovician trilobites from the Marathon uplift, Texas: Jour. Paleontology, v. 28, p. 249–285.

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FIGS. 1–4, DECEMBER, 1958

TIDAL ACTION AS A CAUSE OF CLAY ACCUMULATION[1]

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ABSTRACT

The tidal flats on the southeastern border of the North Sea are developed behind a chain of barrier islands. In this area the grain size of the sand decreases from the inlets towards the inner shores and the tidal watersheds behind the islands. Likewise the clay content increases, so that muddy sands and even sandy muds are formed. This condition is explained by the action of tidal currents combining with other, mainly biological phenomena. Pellets and flakes are formed and these are carried inwards in consequence of the "settling lag effect" and the "scour lag effect." In estuaries and tidal lagoons similar conditions may be responsible for lateral changes in clay content. In ancient basins such lateral increase in fine grained material may indicate approach to the mainland shore and increasing distance from passes between sandy barrier islands. This study is an elaboration of suggestions offered by Postma (1954). A more detailed account with extended bibliography and full acknowledgements has been given in an earlier paper (van Straaten and Kuenen, 1957).

INTRODUCTION

It has been known for a long time that in the tidal flat area along the North Sea coasts of Denmark, Germany, and Holland the average grain sizes of the sand are smaller than in the adjoining parts of the North Sea. Moreover, they tend to decrease from the inlets towards the inner shores and towards the tidal watersheds (fig. 1) which connect the barrier islands with the mainland. In the same direction the clay percentage increases, especially close to the mainland shore. There much of the deposits is either muddy sand or even sandy mud.

The present configuration of the tidal flat sea (fig. 1) is apparently the result of a combination of deposition in a low area behind the chain of barrier islands and of erosion in the tidal channels. This erosion resulted in the formation of lag sediment: some gravel, shells, clay pebbles, and coarse sands. The bottom of the major tidal channels at and close to the inlets is very rich in such coarse materials. The cross section of these channels is somewhat smaller than would be the case if only fine sand were present because higher bottom velocities can now develop without erosion.

The fact that, passing inwards along the channels, the bottom sediment is found to decrease more or less gradually in average grain size is easily explained as the result of the decrease in this direction of the average and maximum current velocities. In or near the inlets the sediment can contain only a subordinate amount of fine sand because most of the time the bottom material is being winnowed out by the strong currents. Farther inwards, where the currents are weaker, these finer fractions make up a greater percentage of the sediment, owing to two causes. In the first place, greater quantities of fine sand can come to semi-permanent depostion, and in the second place there is a much reduced supply of coarse grains by the flood currents owing to their diminished competency.[2] But the same reasoning cannot be applied to the suspended load entering from the North Sea because it moves with very sluggish currents.

However, several organic factors come into play. In the first place a dense population of pelecypods, mainly *Cardium edule* and *Mytilus edulis*, filter clay from the water and return it in the shape of faecal pellets and pseudo-faeces. These aggregates of clay material (especially the true faecal pellets) and the fragments formed by erosion of old mud or clay beds are comparatively coherent and behave more or less as sand-size grains. On the marshes along the shores various plants catch fine sediment. Then diatoms produce slime that binds clay. Much larger floccules than result from the electrolyte action of sea water tend to form from organic detritus to which clay par-

[1] Manuscript received February 7, 1958.

[2] An interesting article on this subject was published by Postma (1957).

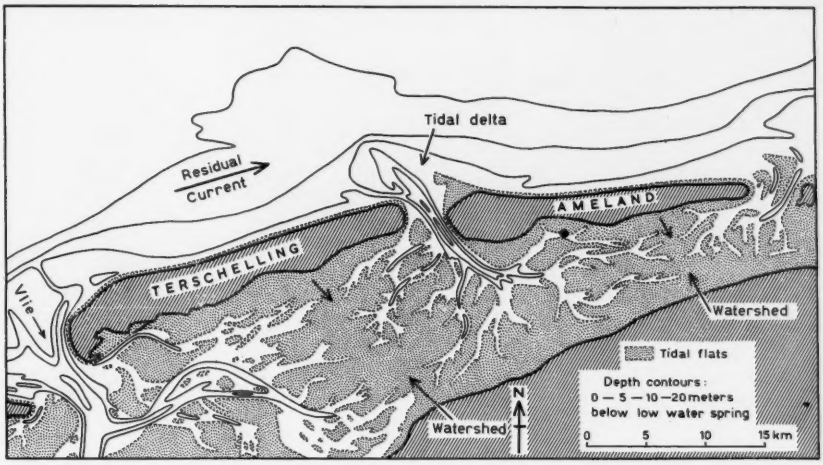

FIG. 1.—Map of the central part of the Dutch Wadden Sea, showing the general relations between barrier islands, outer tidal deltas, inlets, main channels, tidal flats, and watersheds.

ticles adhere. These various larger particles settle much faster than the fine floccules of the open sea. In this manner clay becomes mixed with the sand deposits.

As the density of the mollusc population and the efficiency of the other factors tend to increase inwards[3] it has been generally assumed in the past that this accounts satisfactorily for the augmentation in the same direction of the clay content in the sands. One could suppose that if a new tidal area were to come into existence, the mud admixture to the sand would at first increase owing to the organic influences. This would happen at the expense of the total quantities of suspended mud in the tidal flat sea. Under such conditions the average concentration of suspended matter would therefore become lower than in the open sea. But rolling of pellets and fragments together with sand as a result of tidal currents and wave action must cause abrasion of the "clay sand," thus causing part of the clay to be resuspended. A steady state would be attained when this gain in suspension compensates the loss due to the mud-condensing factors. The concentration in suspension would then be equal to that in the open sea.

However, the periodical occurrence of storms prevents the establishment of such a steady state. During storms there must be a great loss of mud from the tidal flat area. The amounts of suspended mud become much higher under these circumstances than the average in the open sea. The ensuing decrease in clay content in the bottom will cause a shifting of the equilibrium during the following calm weather period. Recuperation of deposited clay by pellet formation in the calm periods must then entail a loss from the suspension. One should therefore expect the water of the tidal sea to be clearer than that of the North Sea except during storms.

In reality a different situation is found. Postma (1954) showed that during calm weather the concentration of the suspension is also much higher in the Wadden Sea than in the North Sea, especially close to the shores. This fact was already demonstrated before him by Gry (1942) and is familiar to

[3] The most abundant pellet-producing species, *Cardium edule* and *Mytilus edulis* live mainly on the tidal flats. Going inwards from the inlets the area covered by the flats is seen to increase gradually in comparison to the area covered by the channels. Hence, the influence of the formation of pellets must also augment in inward directions, except close to the shores where the elevation of the flats becomes relatively great and where the populations decrease because the periods of inundation by the tides become too short.

all who have worked in the area. Postma also found that fresh water from sluices on the Wadden Sea coast is quickly exchanged with the North Sea by the in- and outflowing tidal currents. Hence, the suspended load must also undergo this diffusion and loss to the open sea. The fact that the increase in concentration of suspended sediment towards the land is maintained indefinitely proves that some contrary mechanism must be active in keeping the fine material stored in the inner waters in spite of loss by diffusion.

Postma suggested the following mechanism. When the flood current gradually decreases in velocity towards the time of high water, there comes a moment at which a given particle of the suspended load can no longer be retained and is allowed to drop to the bottom. But a certain amount of time elapses while the particle travels to the bottom and in the meantime it is carried further inwards on the slackening current. It is thereby taken to a spot where the average current velocity is less than at the point where it began to drop out, owing to the general decrease in average current velocities from the inlets inwards. This happens to all particles of the suspended load. Therefore the ebb current is not able to remove all the deposited particles. In the long run this should lead to the observed distribution of fine grained sediments in the Wadden Sea. Postma's idea will be elaborated in the following pages.

THE LAG EFFECTS

The usual manner of studying tidal currents and their action is to ascertain the varying velocity and sediment load at fixed points. This leads to complications in an environment in which the average current velocities vary from place to place. Examples taken from the present area are as follows. At the moment that the flood current reaches its maximum velocity at a given point, the water particles that pass over this point have already started to slow down. A decrease in suspended load may be noted by an observer at a fixed point at a moment when the current velocities of the passing water are still on the increase, etc. A much simpler picture is obtained by following in mind a certain mass of water as it moves in and out with the tide.

A number of simplifications have to be made, but these probably do not alter the general trends significantly. It will be assumed in the first place that current velocity is equal at all points in a channel section; in the second place that the tidal curve at all points is a symmetrical sinus curve; in the third place that high and low water occur at the same moments throughout the tidal sea; in the fourth place that the average current velocity decreases inwards proportionally to the distance between inlet and coast or watershed.

The shape of the curves representing the relation between velocity and position for a particle of water on these assumptions was calculated at the request of the writers by Dr. R. Dorrestein and is shown in figure 2. The tangent to these lines starts at the inner shore of the Wadden Sea (or the watershed) and meets each curve at the point attained by the particle in question at half tide. The higher velocity and the greater distance lie on the seaward side of this point. A water particle moves in and out on one such curve.

With the aid of these curves the action of the current on a particle of sediment can be traced. The particles in suspension are continuously exchanging places owing to turbulence. This will be ignored and the treatment will be as if the same individual particle were holding its position. There may even be some interchange with particles lying on the bottom, but this is reduced to a minimum by the fact that the current velocities required for erosion of bottom particles are always greater than the velocities at which these same particles can be deposited from suspension. Likewise, the treatment will deal with a particle at average (weighted) depth.

Two phenomena appear to be of primary importance for the accumulation of fine grained material from the inlets towards the shores. The first one is the circumstance, already mentioned by Postma (see above), that particles settling from a slackening current are not deposited vertically below the place where they start to drop out from the suspension, but that they are carried along some distance before reaching the bottom. In the following this will be called: "settling lag." The other phenomenon referred to in the preceding paragraph is based on the difference between the maximum cur-

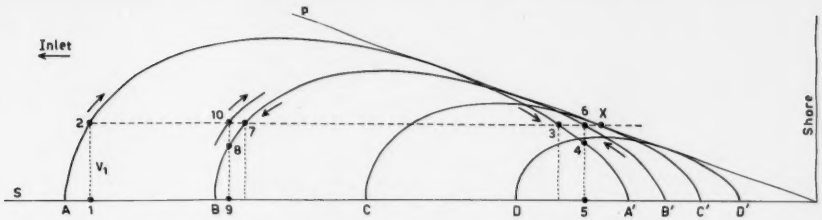

FIG. 2.—Settling lag effect. Diagram showing the velocities (v) with which different water masses move with the tides at each point along a section through the Wadden Sea from somewhere in the direction of the inlet (left) to the shore or towards the watersheds (right). The curves apply only to idealized, average conditions. Scour lag is supposed to be zero.

A sediment particle taken into suspension at point 1 by a flood current of increasing velocity, starts to settle towards the bottom at point 3, when the current velocity drops again below the value attained at point 1. In consequence of the settling lag the particle reaches the bottom later, at point 5, when the current velocity has meanwhile diminished to the value represented by the vertical 4-5. After the turn of the tide it cannot be eroded by the same mass of water, because this attains the required velocity only later, when it has reached a point situated more towards the inlet. The sediment particle is therefore eroded by a more landward mass of water (curve B-B') and taken along in the direction of point B. At point 7 it starts to drop out of suspension. It reaches the bottom at point 9. During one tidal cycle the particle has therefore shifted from point 1 to point 9.

rent velocities allowing sedimentation of suspended particles and the minimum velocities required to erode the same material from the bottom. It has been investigated in detail by Hjulstroem (1935, see also Sundborg, 1956). The smaller the grain size the greater is this difference. This phenomenon will be called "scour lag."

First the effect of the settling lag will be considered by itself. It will therefore be temporarily supposed that the scour lag effect is zero. Let it be assumed that a particle is of such size that it requires the velocity, v_1, to be held in suspension by turbulence (fig. 2). It is lying on the bottom at point 1 where the foregoing ebb current dropped it. As soon as the passing flood current has attained the speed v_1 the particle starts to travel inwards. On reaching point 3 the current has slackened to the velocity at which the particle begins to settle. During the subsequent travel to the bottom, however, the surrounding water is still carrying it inwards. The distance covered during this settling lag depends not only on the manner in which the velocity decreases, but also on the depth (not shown in the diagram). It will be assumed that the velocity curve (A-A') is followed until the point 5 on the bottom is reached where the particle in question comes to rest.

When the water which surrounded the particle comes back on the following ebb current, it is still moving too slowly to pick the particle up. The latter remains on the bottom, until water of sufficient velocity starts to pass. This water belongs to a curve (B-B') situated further inwards. At point 7 it drops the particle considered. Owing to the settling lag it is taken a certain distance further seaward, but it can never land on the bottom beyond point B. In the diagram it is assumed that it attains the bottom at point 9. In the course of one tidal cycle this particle has therefore travelled inwards from point 1 to point 9. Some complications arise from the circumstance that the average depth of the water masses moving to and fro with the tides is much larger at low tide than at high tide (see fig. 3). The reader interested in the effect of these complications is referred to the more extended treatment given by the authors in 1957.

Each jump back and forth brings the particle closer to the shore. Soon the flood current will deposit it at a spot so far inwards (to the right of point x in fig. 2) that the ebb current there does not attain sufficient speed to lift it. The critical velocity v_1 then lies above the tangent p (fig. 2). The particle has undergone "final settling lag." There it will remain, until a stronger tidal cycle, or waves, or scour by a moving gully succeed in raising it. Another possibility is that the particle later falls apart or is abraded to form normal marine clay floccules.

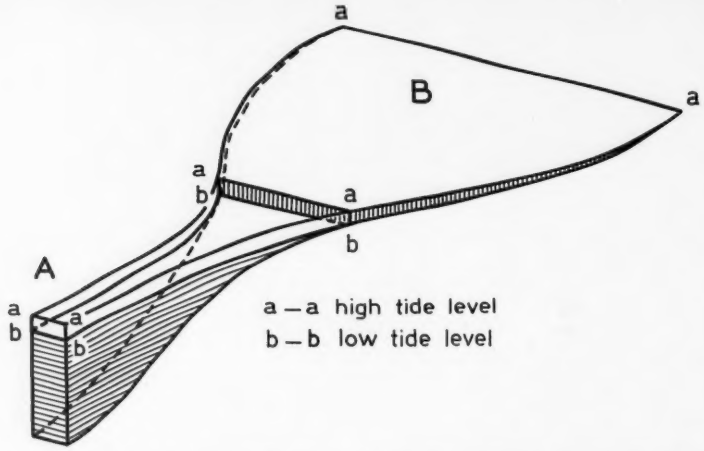

FIG. 3.—A large part of the water in the Wadden Sea is alternately spread out horizontally (*B*) and piled up in narrow deep channels (*A*). At the end of the flood tide most of the settling sediment reaches the bottom because of the shallowness of the water in the area *B*. The quantity of sedimentary material that reaches the bottom at the end of the ebb tide is smaller, owing to the greater depths at *A*.

The effect of the scour lag combined with that of the settling lag is illustrated in figure 4. It is compared with the effect of the settling lag alone. The difference between the scour velocity and the minimum transporting velocity is represented by v_2 minus v_1. A particle which lies on the bottom at point 1 and which is subject to both the scour lag and the settling lag effects has to wait a little longer before it is taken into suspension by the accelerating flood current (curve *A*) than another hypothetical bottom particle which lies at the same point but which is unaffected by the scour lag phenomenon (curve *B*). Towards the end of the flood it is therefore redeposited on the bottom at a point (5), which lies slightly seaward of the point (5′) where the other hypothetical particle comes to land. However, during the beginning of the subsequent ebb tide the resuspension of the normal particle is also delayed with regard to that of the hypothetical particle. Whereas the hypothetical particle returns seaward with the ebb current along curve *C*, the normal particle travels back with a water mass that comes from further landward: curve *D*. Owing to the asymmetry of the curves and to the fairly rapid inward decrease of the travelling distances, the normal particle comes to rest at the end of the ebb tide at a place that lies much more landward than the place where the hypothetical particle reaches the bottom. Hence, it is seen that not only the settling lag, but also the scour lag phenomenon plays an important part in the accumulation of fine grained sediment towards the interior of the Wadden Sea.

INSIGNIFICANCE OF CAPACITY

In the above treatment of lag effects emphasis has been entirely on the competency of the currents, for it has been assumed that a particle is raised as soon as sufficient velocity of the water has been reached. If the amount of sediment to be raised is large or if the current is loaded to near its capacity, there would be a time lag for scour to take effect. But in the area under consideration the amounts of suspended sediment are not large. The only suspendable matter that is available to the currents when these start to run after slack water is that which lies on the bottom and which is caught between those larger grains which are set in motion as bottom load. As the capacity for bottom load is limited, only a minute fraction of the enormous masses of sand in the tidal sea is set in motion. Hence, only a very small amount of clayey matter is set free, an

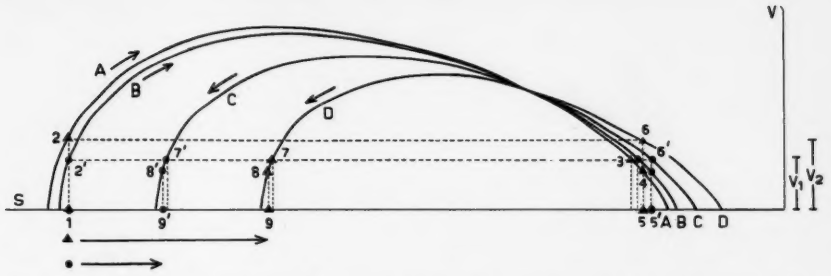

FIG. 4.—Settling lag effect compared with the combined effects of settling lag and scour lag. For explanation see text.

amount very far short of capacity. The consequence is that mud particles are taken into suspension as soon as the current attains the necessary velocity to raise them or to roll away the protecting sand, so that they start to move almost immediately when the necessary competency has developed.

COMPLICATIONS CAUSED BY DIVERGENCE FROM THE POSTULATED IDEAL CIRCUMSTANCES

Matters are complicated in nature by local disagreements with the postulated ideal tidal currents and because flow along the bottom is slower than the average of the cross section. In some localities, for example, the flood current develops a higher maximum velocity than the ebb current. This must tend to enhance the action of the lag effects. At other places, however, the ebb current is relatively stronger and the result will detract from the lag effects. There are as yet insufficient hydrographic data to show whether the former or the latter condition is more widely distributed.

Another complication is that the suspended particles may be moved by bottom traction before and after being moved in suspension. However, the distances travelled in this manner must be small compared to the transport in suspension and can be ignored in first approximation.

The most significant factor which has been neglected so far in the treatment of the lag effects is the action of wind and waves. This means that the outline given above applies only to calm weather. The influence of wind is twofold: to generate waves and to alter the flow of the tidal currents.

The action of waves results in a powerful churning up of mud from the bottom in shallow water, that is mainly on the tidal flats, when these flats are covered by the tides. Few measurements of suspended load have been carried out during storms except close to the mainland coast. But there are plenty of qualitative observations to show that the amounts of suspended clay are a high multiple of what is seen in the North Sea or during calm weather in the tidal area. This great increase in the density of the suspension must necessarily lead to a much stronger gradient between shore and inlet, since the area covered by the flats decreases with decreasing distance from the inlets. This, in turn, must result in strong losses of mud from the tidal sea to the North Sea.

The loss is reinforced by the second influence of the wind. The strongest winds in the area blow from westerly directions. They raise the water level along the North Sea beaches of the barrier islands and increased amounts of water enter the inlets during flood tide. This is especially the case when the winds come from the west (southwestern part of Wadden Sea) or from the northwest (central and eastern parts). Owing to the shallow depths in the Wadden Sea, large masses of water can be piled up under the influence of such storms. When the water level in the North Sea subsides again to normal at the end of the storms, the slope of the water surface becomes very steep during ebb tide. The ebb currents may then reach more than twice their normal velocities, carrying with them great quantities of mud churned up by the waves.

THE MUD BALANCE IN THE WADDEN SEA OVER LONG PERIODS

Over a year or a few years the losses consequent on storms will roughly balance the gain by the lag effects during periods of calm weather. In the long run there are probably trends of loss or gain, dependent in part on relative rise or fall of sea level, climatic or biological changes, variations in supply of sediment, and human activities (reclamation of land and fishing of shells).

The available amounts of clayey material and the volume of sand moved during a tidal cycle are small compared to the vast area of the tidal sea. Hence adjustments to altered conditions need a long time to take effect, as was found after the construction of the great Zuiderzee dyke. For this reason it is not possible to discover whether gain or loss is in progress at present. Measurements of water movements and suspended load giving quantitative results for the whole area are hardly feasible because of the predominant influence of storms. Yet advance towards closer understanding is possible. A larger number of simultaneous observations on suspended load at a few points between inlet and shore are urgently needed, and also data on velocities and load obtained from ships drifting in and out with the current. It would also be extremely useful to gain more information on the amount of sediment deposited and raised again at different points in gullies and on flats.

IMPORTANCE OF LAG EFFECTS FOR OTHER AREAS

According to the view developed in this paper the accumulation of clay results from the formation of flakes, pellets and fragments which are carried in suspension part of the time. In consequence of their settling on the bottom during the slack water stage of high tide they are bypassed during the first stages of the following ebb by the water that surrounded them and are finally raised in a mass of water which comes from closer to shore.

The most important feature of a tidal flat sea in this respect is the gradual decrease in current velocity away from the inlet. It appears possible that similar action occurs in other environments like estuaries[4] and tidal lagoons, provided the clay material forms suitable aggregates and the average current velocities decrease away from the open sea. In river estuaries part of the clay is supplied by the river. This matter flocculates on meeting sea water. Still larger floccules are formed by the sticking together of finely divided clay material and organic detritus floating in the water. The estuarine circulation (salt water undertow) enhances deposition of this material on the channel floors in the river mouth. A spate may wash this accumulation out to sea. In the Dutch Wadden Sea all clay is carried in from the open sea as floccules with or without a substratum of organic material.

It is assumed in many studies of ancient deposits that a gradual lateral decrease in grain size of sand accompanied by increase in clayey material implies a growing depth and distance from the shore. In the tidal flat environment the opposite is the case, for the grain size becomes less and the clay content increases as one passes from the inlets communicating with the open sea towards the inner shores. It may prove useful in litho-facies analyses to keep this possibility in mind.

[4] An important paper on the high contents of suspended matter ("bouchon vaseux") that are found in the estuary of the Gironde (France) was written by Glangeaud (1939). A huge amount of information on the sediment movements in the Loire estuary (France) has been assembled by L. Berthois. A series of short notes was published by this author. For a summary of his results see Guilcher (1956).

REFERENCES

GLANGEAUD, L., 1939, Le mouvement des sédiments et la formation des bancs, seuils et mouilles dans la Garonne et l'estuaire de la Gironde: Congr. Int. Union Géod. et Géoph., Washington 1939, Comm. de Potamologie, Question 3, Rapport 6 (14 p.).

GRY, H., 1942, Quantitative Untersuchungen über den Sichstofftransport durch Gezeitenströmungen: Folia Geog. Danica, II, No. 1, 138 p.

GUILCHER, A., 1956, Les travaux de L. Berthois sur l'estuaire de la Loire: Revue Norois, No. 9, p. 89–90.

HJULSTROEM, F., 1935, Studies on the morphological activity of rivers as illustrated by the River Fyris: Upsala Univ. Geol. Inst. Bull., v. 25 p. 221–527.

POSTMA, H., 1954, Hydrography of the Dutch Wadden Sea. Thesis Groningen. Arch. Néérl. Zoologie, X, 4e Livraison, 106 pp.

POSTMA, H., 1957, Size frequency distribution of sands in the Dutch Wadden Sea: Arch. Néerland. de Zoologie. t. XII, p. 319–349.

STRAATEN, L. M. J. U. VAN AND PH.H. KUENEN, 1957, Accumulation of fine grained sediments in the Dutch Wadden Sea: Geol. en Mijnb., 1957, p. 329–354.

SUNDBORG, A. (1956), The river Klarälven, a study of fluvial processes: Geog. Ann. Arg. XXXVIII, p. 125–316.

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FIGS. 1–3, DECEMBER, 1958

FRESH-WATER ENVIRONMENT OF DEPOSITION OF PRECAMBRIAN BANDED IRON FORMATIONS[1]

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ABSTRACT

Deposition of the banded silica and iron formations, which are typical of the middle "Huronian" rocks of the Lake Superior district, can be accounted for as follows. The region was in a very mature stage of geomorphic development, and the climate of the region was sub-tropical to warm-temperate, with moderate to high rainfall. Iron and silica were the principal products of weathering, being derived alternately during the cooler and warmer parts of the year. The environment of deposition was a large fresh-water lake, low in nutrients and thus having a relatively low organic productivity, and it was of sufficient depth to permit development of density stratification of the water during the summer. The lower water layer, in summer, was isolated from the atmosphere and had a slightly reducing and acid condition; iron was kept in solution in a reduced state but silica was deposited. During the winter the entire column of water in the lake circulated and it was oxidizing and alkaline, causing precipitation of the iron. Any of the iron minerals common to the banded iron formations could be deposited in this environment, because the stability fields of these minerals include the ranges of Eh and pH which occur in this type of lake.

INTRODUCTION

The banded nature of the Precambrian iron formations which consist mainly of alternate layers of chert and siderite, or chert and hematite, seems to record a process of sedimentation which was periodic. The annual temperature cycle of fresh-water lakes, with its effects on water stratification and chemistry of the lake waters, under certain climatic conditions, provides a mechanism for rhythmic deposition of silica and iron.

The writer suggests that the combination of the presence of large, deep, fresh-water lakes with the annual cycle as developed in a subtropical or warm temperate climatic zone, and the existence of the watershed area in a state of very mature geomorphic development, provided all of the conditions necessary for deposition of the Precambrian banded silica and iron formations. This particular combination of factors may not have been repeated since Precambrian time.

The direct contribution of iron and silica to the basins of deposition by volcanic activity is not considered to have been necessary for the deposition of the iron formations. The presence of basic rocks in the watershed areas would have insured adequate source materials. The earth's atmosphere is assumed to have had approximately the same composition during the deposition of the banded iron formations as it has today.

The present paper relates to the banded chert and iron-mineral formations of middle "Huronian" type, and not to any others, such as the iron sulfide-bearing formations which are commonly associated with dark-colored shales and carbonate rocks.

Several writers have adequately demonstrated that the banded iron formations were deposited as chemical sediments, and some have proposed a fresh-water environment of deposition for these rocks. No one, however, has thus far proposed a generally acceptable mechanism of deposition involving a fresh-water environment.

A brief review of the literature is given in the following paragraphs, to set up a framework within which the problem may be considered. This is followed by descriptions of the processes operating in fresh-water lakes, particularly in relation to annual variations in the chemistry of their waters and to the deposition of iron and silica. Weathering processes under the climatic and geomorphic conditions which influence the delivery of iron and silica to a basin of deposition are considered. Finally, a particular combination of these processes is proposed to have existed during part of Precambrian time to account for the banded iron formations.

[1] Presented May 6, 1957, at a meeting of the Institute on Lake Superior Geology, at Michigan State University, East Lansing.

REVIEW OF THE LITERATURE

The sedimentary origin of the middle "Huronian" banded silica and iron formations, in the Lake Superior region, was stated by Van Hise and Leith in their monograph (1911, p. 500). This conclusion was based on the facts that the iron formations are interbedded, in many places conformably, with other sedimentary formations—quartzite, conglomerate, slate, and limestone; they contain recognizable sedimentary material, such as iron carbonate, greenalite, shale, sand, and conglomerate; and the field relations of the rocks obviously indicate a sedimentary origin.

These iron-bearing formations were regarded by Van Hise and Leith as *chemical* sediments because (1) they consisted originally [this is an unproven conclusion] of iron carbonate and ferrous silicate and possibly some iron oxide, similar to substances known elsewhere to be deposited as chemical sediments; (2) they may be synthesized in the laboratory by simple chemical reagents which were probably present [?] where the iron-bearing rocks were formed; and (3) they usually lack fragmental particles.

Because Van Hise and Leith (1911, p. 505–506) believed that the rocks of the iron-bearing series contain a much higher percentage of iron and silica than are contained in the possible source rocks from which they might have been derived by ordinary processes of weathering, they supposed that some unusual source of material was available. On page 516 they concluded that the source of the iron was in the large masses of contemporaneous basic igneous rocks, and that, "the iron salts have been transferred from the igneous rocks to the sedimentary iron-bearing formations partly by weathering when the igneous rocks were hot or cold, but the evidence suggests also that they were transferred partly by direct contribution of magmatic waters from the igneous rocks and perhaps in small part by direct reaction of the sea waters upon the hot lavas."

Gruner (1922, p. 446) marshalled evidence against the direct contribution of iron and silica by magma, and suggested (p. 457) that the source of these materials which formed the Biwabik Formation was a large land area in North America that was covered largely by greenstones and basalts. He suggested that the climate was humid and probably tropical or subtropical, with abundant land vegetation of a low form which resulted in rapid decay of the rocks and concomitant solution of large quantities of iron and silica.

Moore and Maynard (1929, p. 276) demonstrated that carbonated water is able to dissolve sufficient iron and silica from a basic terrane to form a large sedimentary iron deposit, and that organic matter and inorganic acids may cause much iron and silica to go into solution. Further, they concluded that the iron of the large sedimentary iron formations had been transported principally as a ferric oxide hydrosol, stabilized by organic matter, and that the greater portion of the silica was transported as a silica hydrosol. Data were cited (p. 286–292) showing that some present-day streams carry sufficient quantities of iron and silica to provide the materials for deposition of large iron-silica deposits.

Laboratory experiments (Moore and Maynard, 1929, p. 524) indicated that banding of the deposits could be due to a differential rate of precipitation of the iron and silica combined with the influence of seasonal changes causing varying quantities of the two materials to be brought into the basin of deposition at different periods throughout the year.

These authors stated (on p. 510) that "a perusal of the literature gives no adequate explanation of the characteristic banding . . . " and in their conclusions (p. 524–527) they gave no specific natural mechanism for production of the banding. The senior author (Moore) stated a preference for direct contribution by igneous activity to account for the silica and iron deposits.

Leith (1934, p. 158) made the observation that "the Lower and Middle Huronian series, consisting of quartzites, slates, limestones, and iron formation, making up less than a quarter of the pre-Cambrian sediments of this region, have usually been regarded as marine, mainly on the ground of their good assortment, uniformity over wide areas, evidence of deposition from standing water, and absence of distinctly continental characters. On the other hand, they are, in the main, shallow water deposits, and might well have accumulated in land-locked basins."

Woolnough (1941) praised the contribu-

tion of Moore and Maynard (1929), but rejected Moore's opinion that direct magmatic contribution of silica and iron was necessary. Woolnough proposed that the marine environment could not provide conditions necessary for precipitation of the banded silica and iron formations. He postulated that these formations were deposited in basins separated from the sea, most probably occurring in regions of very mature geomorphic development. The mature stage of erosion of the watershed would provide for a minimum of clastic sedimentation and a dominance of silica and iron in the material transported to the site of deposition. Woolnough stated (p. 477) that, "Banding is easily explained as due to successive accessions of solution readily accounted for by seasonal, but not necessarily annual cycles of rainfall." The rhymic deposition is thus considered a result of pulsations in the amounts of silica and iron delivered to the basin.

Sakamoto (1950, p. 458–463) also stated that the materials in the banded iron formations could be derived by mature weathering on a land surface in an appropriate climate, and he stated that the view that the iron was derived from submarine volcanoes, or special volcanic rocks, is quite untenable. The mechanism of precipitation of iron and silica postulated by Sakamoto involved weathering under monsoon-like climatic conditions, and periodic delivery of the iron and silica to basins which were wide but shallow and were separated from the open sea by low barriers. Sakamoto supposed that iron was delivered to the basin by surface runoff during the wet season, when the basin water was cool, acidic, and oxidizing, but that the iron remained in solution during this season; that silica was delivered to the basin by ground water, during the dry season, when the basin water was warm, alkaline, and less oxidizing, but that the silica was not precipitated at this time. He stated that iron was precipitated during the dry season (when conditions were less oxidizing) and that silica was precipitated during the wet season. The chemistry of the lake waters proposed by Sakamoto is subject to serious doubt in view of limnological information which is cited on subsequent pages.

Tyler and Twenhofel (1952) expressed the opinion that the formations described by Van Hise and Leith (1911), and listed on a foregoing page, actually are in part time-equivalents and grade into each other, rather than being entirely successive. Thus, it appears that quartzites, slates, and iron formations may have been deposited simultaneously in different parts of the same basin. If this were true, it would not seriously affect the interpretation that the geomorphic condition of the region at the time of deposition was one of maturity. The constituents of the sediments were mainly quartz sand, clay-sized material, and silica and iron, all products of extreme weathering. The coarser particles, sand and even larger particles, could be transported by streams of low gradient but large discharge.

The proposal of Sakamoto (1950), summarized in foregoing paragraphs, was not well received by Tyler and Twenhofel (1952, p. 136–137), who pointed out that for various reasons it fails to explain the uniqueness of all the Precambrian banded iron formations.

Tyler and Twenhofel noted that little or no magnesium or calcium carbonate is associated with the iron carbonate deposits of the Huronian of Michigan, and considered it obvious that the waters in which the siliceous siderites were deposited could have contained little magnesium or calcium. They concluded that the basin of deposition must have had no or very restricted connection with the open sea, so that the waters in the basin must have had a composition approximating that of the indraining streams. They stated that the iron and silica deposits are of fresh water and not of marine origin. Further, they stated that the segregation of the iron and silica into bands seems to be a primary feature and indicates some form of cyclic deposition, but that the banding could not be related to volcanisms because the necessary regular periodicity cannot be assumed in volcanic activity.

Twenhofel (in Tyler and Twenhofel, 1952, p. 136–137) expressed the opinion that the uniqueness of the banded silica and iron formations in the Huronian must depend on a difference in the composition of the earth's atmosphere between Precambrian and later geologic times. He seemed to imply that an atmosphere with a lower oxygen content and richer in carbon dioxide

was necessary to account for the deposition of iron carbonate. In anticipation of data on fresh-water lakes, to be presented in a subsequent part of the present paper, it may be pointed out that the lower layer of lake water in the summer is insulated from the atmosphere and generally is deficient in oxygen and may have a high carbon dioxide content.

Krumbein and Garrels (1952) considered quantitatively the behavior of iron, and concluded that hematite is deposited at oxidation-reduction potential and pH values above a boundary which extends from an Eh of +0.16 and a pH of 6, to a point at an Eh −0.22 and pH of 9; that siderite is deposited below this boundary but above a boundary which extends from Eh −0.11 and pH 6, to a point at Eh −0.31 and pH of 9; below this boundary pyrite is deposited. They stated that the boundaries between the fields of stability of hematite, siderite, and pyrite are essentially independent of temperature, pressure, and composition of the natural water system from which they precipitate. The amount of a particular mineral that will precipitate depends upon the amount of the constituents available but a change in deposition from one mineral to another will not take place unless there is a change in the Eh or pH of the environment.

In normal sea water, where abundant calcium is present, calcite is deposited at a pH greater than about 7.8, throughout the entire range of possible Eh values. These calcite deposits will dilute and mask any iron precipitates, and for this reason Krumbein and Garrels limited the field of deposition of iron-rich sediments to a pH range below 7.8. While Krumbein and Garrels gave attention mainly to a normal marine environment, they stated that variations in salinity, from essentially fresh water through brackish water to the normal salinity of sea water would have only a minor effect on the mineral stability fields. In those fresh-water lakes which are low in calcium iron deposition in significant quantities may be expected at any attainable pH value above 6, as long as sufficient iron is available.

James (1954) recognized oxide, carbonate, silicate, and sulfide facies of iron formations. He stated that these facies reflect certain aspects of the chemistry of the depositional environments. The major control, at least for the oxide, carbonate, and sulfide types, probably was the oxidation potential.

James (1954, p. 243) argued for a marine environment of deposition of the banded silica and iron formations as follows:

"1. The iron-formation and associated strata possess none of the attributes, such as predominance of coarse clastics and poor sorting, traditionally assigned to continental deposits." The absence of these "continental" attributes does not preclude deposition in a large body of fresh water.

"2. The major iron-formation units . . . are sandwiched between lower Huronian quartzite and dolomite and upper Huronian graywacke, slate, and volcanic rocks. The lower Huronian is unquestionably marine, and the upper Huronian . . . is one of the classical assemblages found in geosynclinal tracts such as the Mesozoic of the Pacific Coast, where the weight of evidence indicates marine environment." Even if the underlying and overlying rocks are unquestionably of marine origin (and there is room for some doubt that all of them are), the middle Huronian rocks are not necessarily marine.

"3. The pyritic slates associated with iron-formation proper in some areas may be of significance. . . . The availability and fixation of . . . a vast quantity of sulfur . . . suggests that the basin of deposition was connected to the open sea. . . . " These rocks may be accepted as marine deposits, but this does not prove that the typical banded silica and iron formations of other areas are of marine origin.

"4. Younger iron-rich strata, such as the Clinton formation, are similar in some important respects to the Precambrian iron-formations. . . . The marine origin of these beds is demonstrated beyond question by abundant fossils." These younger strata are not similar to the middle Huronian iron formations in the important matter of being banded silica and iron formations; therefore the marine origin of the Clinton strata does not prove marine origin of the banded formations.

The specific environment postulated by James, restricted basins which were separated from the open sea by thresholds that inhibited free circulation and permitted development of abnormalities in oxygen po-

tential and water composition, could account for the kinds of minerals occurring in the iron deposits but not for the banded nature of the iron formations.

Alexandrov (1955) reconstructed the geochemical environment favorable to the development of the Precambrian banded iron formations, and illustrated the reconstruction with results of experiments with the leaching of iron oxide and silica at different temperatures, at different pH ranges, and in the presence of certain elements in solution. He suggested that the banding of silica and iron minerals was caused principally by the selective weathering of the soil in different seasons; that seasonal changes of temperature, amount of precipitation, and pH caused the Precambrian soil to yield alternately solutions carrying to the basin of deposition almost exclusively silica during the warm season and chiefly iron oxide during the cool period of the year.

Goodwin (1956), in discussing the Gunflint Iron Formation, objected to weathering as a source of iron and silica on the following grounds: (1) a complete lack of maturely weathered *residual* material in the Gunflint area; (2) the difficulty of transporting ferric iron in surface waters to the site of deposition followed by reduction to the ferrous state (as prevails in the Gunflint) without the aid of abundant organic matter (which is quantitatively absent in the Gunflint); (3) the improbability of an "abnormal" reducing atmosphere during Gunflint time . . . ; and finally (4) the absence of Gunflint-type iron formations from all rocks younger than Precambrian in age.

These objections may be answered as follows: (1) the residual soils of the source areas were destroyed in a later cycle; (2) organic matter may have been abundant in the basin of deposition without having been preserved in the sediments, because the organic matter had to be oxidized in the process of reduction of the iron. This is well illustrated by the bottom sediments in deep water in the present Great Lakes (see page 427). (3) An "abnormal" reducing atmosphere is not required. The hypolimnion of a monomictic or dimictic lake is insulated from the atmosphere and may produce its own reducing environment. (4) The absence of Gunflint-type iron formations from all rocks younger than Precambrian in age could also be used as an argument against the hypothesis of direct magmatic contribution of iron and silica.

Oftedahl (1958), in a paper dealing with various kinds of ores and their possible sources in volcanic emanations, revived the Van Hise theory of origin of the banded formations by direct contribution of iron and silica from magmatic emanations to the basin of deposition. He stated that, "The sharp and rhythmic banding which is frequent in iron formations may then be due to periodic, earthquake-governed bursts of iron-bearing gases and the quiet giving off of silicon-bearing gases or hydrothermal solutions in between" (p. 10). This hypothesis remains as a not-impossible mechanism of development of the banded formations, but the present writer regards it as an unlikely one.

Huber (1958) developed new stability diagrams for the iron minerals hematite, magnetite, siderite, pyrite, and iron sulfide, in sea water systems. One of these diagrams is reproduced in figure 1 of the present paper. This is based on the carbonate equilibria as in normal sea water and on total sulfur as in average river and lake water. It shows the siderite zone extending up to a pH of 6 and the magnetite zone beginning there and extending to higher pH values. In his discussion of the environmental control of sedimentary iron minerals, Huber did not consider fresh-water lakes as a possible environment of deposition. However, because salinity has a minor effect on the stability of the iron minerals considered, figure 1 may be used for an approximation of the stabilities of these minerals in lake water.

SUMMARY OF THE PROBLEM

The publications reviewed in the foregoing pages provide a framework for consideration of the history of development of the Precambrian banded iron formations, which is summarized as follows.

The banded silica-iron mineral formations are chemical sediments.

The banded iron formations especially, and some of the rocks with which they are closely associated, are products developed as a result of advanced weathering, probably in a very mature geomorphic terrane.

The iron and silica could have been de-

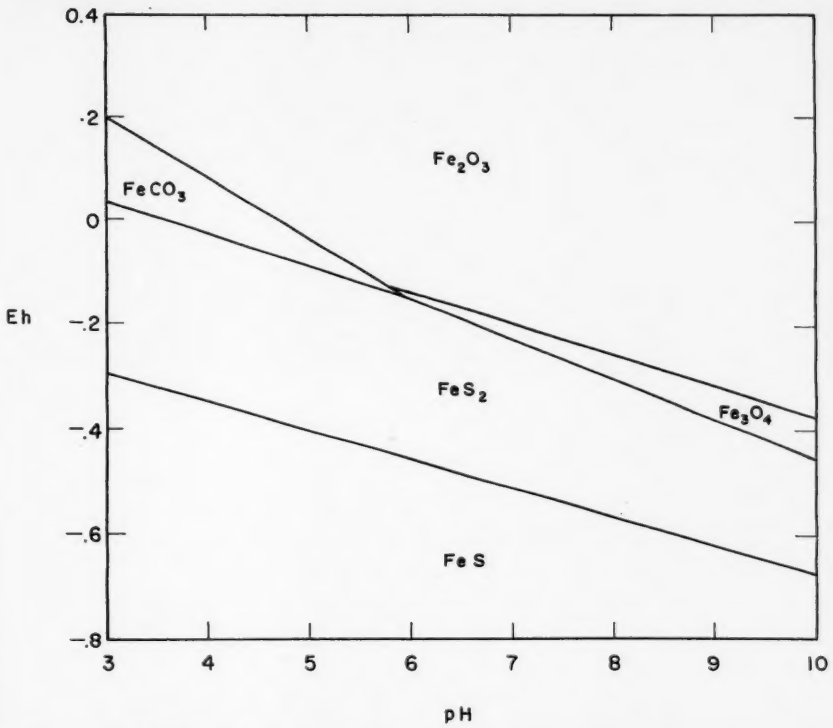

FIG. 1.—Stability fields for hematite, siderite, magnetite, pyrite, and iron sulfide (FeS) with carbonate equilibria as in normal sea water and total sulfur as in average river and lake water. (After Huber, 1958, fig. 5.) Because salinity has a minor effect, this diagram may be taken as an approximation of the stability fields as in fresh-water lakes.

rived by weathering of rocks in the watershed, and direct contributions from magmas or lavas were not required. Iron-rich rocks such as greenstones and basalts were abundant in the source areas, but these are not considered absolutely essential as source materials. Weathering of a varied terrane under appropriate conditions is capable of providing adequate quantities of silica and iron, for transportation to the basin of deposition, to account for the volumes of materials occurring in the Precambrian iron formations.

A seasonal alternation in production, by weathering, of silica and iron is possible, under appropriate conditions of temperature, pH, composition and quantity of surface water.

Some present-day streams are carrying quantities of silica and iron which would be adequate to account for the iron formations; transportation of the materials thus seems to be quite adequately explained.

The environment of deposition was not in normal marine water, but in a basin separated from the sea, according to several writers.

The precipitation of the various iron minerals which occur in the banded iron formations, including hematite, siderite, magnetite, pyrite, and even of hydrous ferrous silicates, is controlled largely by the oxidation-reduction potential and to a lesser degree by the pH of the environment. The Eh and pH values required for deposition of all of these iron minerals are within the

ranges which occur in freshwater lakes.

The principal item which is lacking from the foregoing synthesis pointing toward a fresh-water environment of deposition is a specific and detailed account of the mechanism by which the appropriate chemical environments could be provided to account for precipitation of the various iron minerals and of silica, in alternate layers.

Most geologists concerned with sedimentary processes are familiar with details of the marine environment, and write knowingly of such things as barred basins, euxenic environments and the like. It is the writer's opinion that most geologists are unfamiliar with a large amount of information which is available on fresh-water lake environments. Limnologists, who are primarily zoologists and botanists, have been gathering this information over a period of many years but only summaries of it or occasional references to it have gotten into the geologic literature. Because a precise explanation of the manner of deposition of the Precambrian banded iron formations can be constructed from this body of limnologic knowledge, a rather detailed discussion of it is presented here.

THE LACUSTRINE ENVIRONMENT

The fresh-water lakes of the North Temperate Zone have been studied in greatest detail, and the present discussion is based mainly on the studies of these lakes. Even in these temperate-zone lakes there is a variety of environments. Different lakes have different environments. There are different environments in the same lake at different times of the year, and different environments existing simultaneously in the open waters of the same lake, during a part of each year.

The Annual Temperature Cycle and Its Effect on Density Stratification

Marine water increases in density with a lowering of the temperature until the freezing point is reached. Fresh water, however, attains a maximum density at a temperature of about 4 degrees centigrade and further cooling results in a progressive decrease in density until the freezing point is reached. Lake water is warmed and cooled mainly by exchange of heat through the lake surface. Unlike water in a pot on a stove, which is heated from the bottom, the water in a lake does not respond to the principal additions of heat by circulating. A temperate-zone lake of appreciable depth retains some water in its deepest part which is at or close to the temperature of maximum density throughout the year. The surface water temperatures range from the freezing point (in the winter) commonly to 15 degrees centigrade and to as much as 22 degrees centigrade (in the summer). Circulation of the water is produced mainly by wind stress on the surface, and circulation is limited almost entirely to a relatively shallow layer of water whenever the surface temperatures are appreciably higher or lower than 4 degrees centigrade.

Dimictic Lakes of the Temperate Zone

The annual cycle of temperature and density distribution in a typical lake in the Temperate Zone is illustrated in figure 2. For a brief period in the spring of the year the lake water is isothermal (has the same temperature from top to bottom) at, or close to, 4° C, the temperature of maximum density. Because the density of the water is essentially the same throughout the column, any circulation resulting from wind stress on the surface involves the entire column of water and the phenomenon known as "spring overturn" results (fig. 2A). This complete circulation involves the movement of surface water, whose dissolved gases are essentially in equilibrium with the atmosphere, down to the bottom of the lake and the movement of bottom water to the surface, where it acquires atmospheric gases.

As heat is added to the surface water during the spring that water becomes lighter. In a typical lake in most spring seasons a distinct layer of warmer water develops rather rapidly. When this occurs, the layer of warmer and lighter water can not be forced to greater depths and the wind-stress induced circulation is limited essentially to that layer. This initiates a summer stable condition (fig. 2B) in which the lake remains stratified, with warmer and lighter water of the upper layer (the epilimnion) continuing to circulate and with the lower water (the hypolimnion) remaining at a temperature close to the temperature of maximum density and being isolated from the atmosphere and having little or no circulation. In this

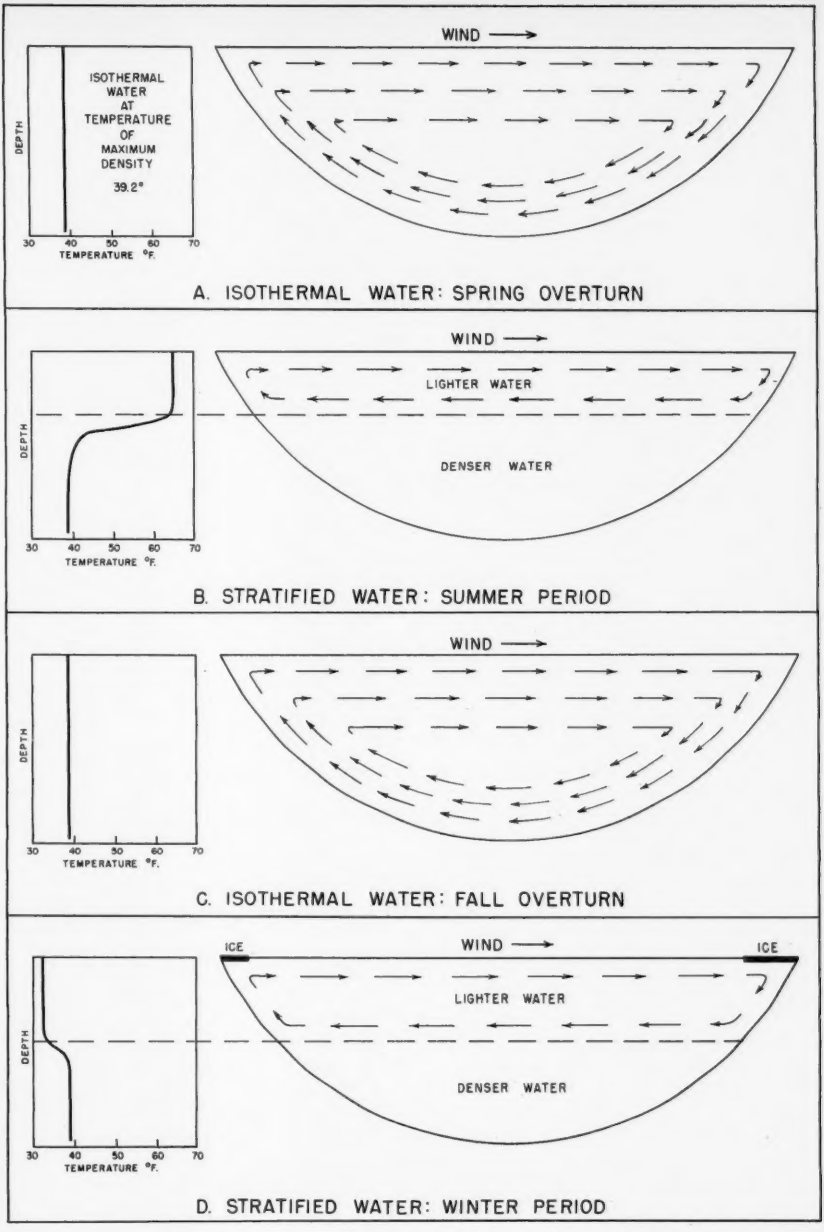

FIG. 2.—The annual temperature cycle in dimictic lakes, or typical deep lakes of a temperate zone. (Reproduced from Hough, 1958, fig. 22, Geology of the Great Lakes, by permission of the University of Illinois Press.)

condition the isolated lower water mass (the hypolimnion) may undergo important changes in its chemistry.

During the autumn there is a net loss of heat from the lake, through its surface, and the temperature of the epilimnion (which remains well-mixed) gradually is lowered until it is close to the temperature of the hypolimnion. As soon as the density differential between the two water masses is small enough, circulation of the entire column of water begins. This initiates the "fall overturn" (fig. 2C), wherein the lake waters are thoroughly mixed and replenished in atmospheric gases.

The condition of fall overturn is ended, by additional loss of heat, when a surface layer of colder water develops. This water, being colder than 4° C, is lighter than the water below it and it can not be forced to greater depths. The winter stable period (fig. 2D) is thus initiated. In this condition the lake remains stratified, with the colder and lighter water of the upper layer continuing to circulate as long as the lake remains unfrozen and with the lower water remaining at a temperature close to the temperature of maximum density and being isolated from the atmosphere and having little or no circulation. If the lake is completely covered with ice, the upper layer of water will be isolated from the atmosphere and will have no appreciable circulation, but it will remain as a distinct layer floating on the denser water below.

The winter stable period is ended when the temperature of the upper layer of water increases to, or nearly to, that of the lower layer. When the density differential between the two layers is small enough, circulation of the entire column of water begins (under the effect of wind stress). This initiates the spring overturn, with which the present account began.

In summary, the typical medium- to large-sized fresh-water lake of a temperate climatic zone has two periods of complete circulation, when the water is isothermal, in spring and in autumn, and two periods of stability due to density stratification. Such lakes are termed "dimictic." During the summer the stability is great but during the winter the stability is slight.

The annual cycle as described in the foregoing paragraphs is somewhat idealized and is a statement based on summaries in textbooks of limnology (see, for example, Welch, 1935, p. 45–46, Ruttner, 1953, p. 32–35, and Hutchinson, 1957, p. 534–540). Variations from the idealized cycle occur, principally involving the effects of rate of heating in the spring and rate of cooling in the autumn and the intensities of wind-stress at these times of instability.

Atypical Dimictic Lakes

The Great Lakes of North America, although lying in the North Temperate Zone, depart somewhat from the idealized temperate-zone lake. The effect of large surface area and considerable wind stress is a greater amount of circulation when the stability of the water is relatively low. As a result, the periods of overturn or complete circulation are of longer duration and the winter stable period is considerably shorter (Hough, 1958, p. 5). The behaviour of the Great Lakes thus approaches that of a typical sub-tropical lake, which is described in the following paragraph.

Monomictic Lakes of the Sub-tropics

The typical sub-tropical lake, according to Hutchinson (1957, p. 535), is a "warm monomictic" lake in which the stable stratification of the summer season alternates with a single annual period of complete circulation, in the winter season (fig. 3). In the idealized type of this lake the water temperature is never below 4° C at any level, and the water circulates freely during the winter at or above 4° C.

A lake in a sub-tropical or a warm-temperate climatic zone may conform to the "warm monomictic" type of behaviour even though the water temperature falls below 4° C, if the lake has a large surface area and is under frequent strong wind stress. This behaviour can be effected by mixing when the temperature (and density) differential between the different levels is low. That is, when in the autumn the temperature of the epilimnion falls to within a degree or two of the temperature of the hypolimnion mixing can begin (under strong wind stress) and mixing can then continue as the temperature of the entire column of water falls to two or three degrees below the point of maximum density. If further cooling does not occur, the lake will continue to circulate in an

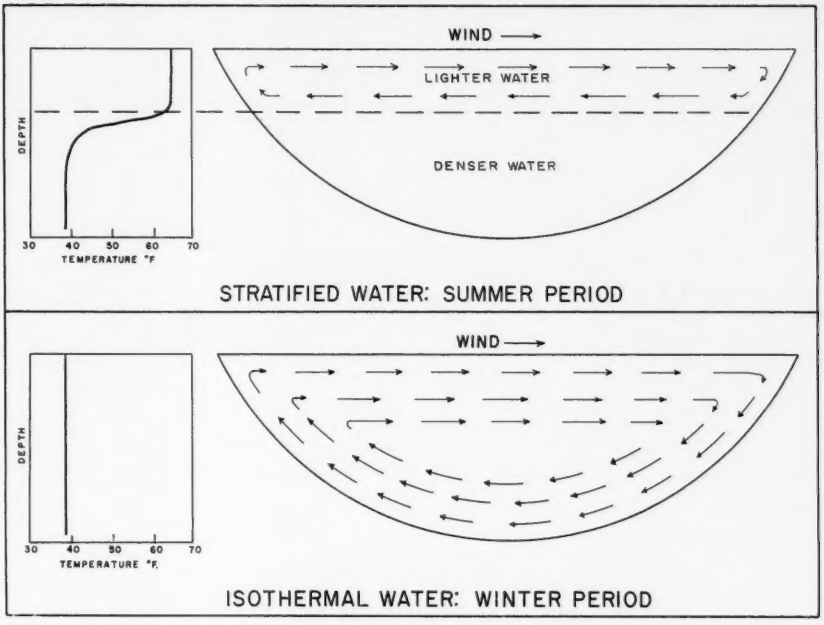

FIG. 3.—The annual temperature cycle in monomictic lakes, or typical deep lakes of sub-tropical and warm-temperate zones.

isothermal condition throughout the colder part of the year.

Some lakes are monomictic in some years, and dimictic in others, depending on the amount of heat lost in the cooler part of the year and on the amount of turbulence during the critical times of low stability of the water column. Tom Wallace Lake in Kentucky, lat. 38°05′ N., is an example of such a lake (Hutchinson, 1957, p. 441).

The annual cycle in monomictic lakes, characteristic of subtropical, and occurring also in warm temperate climatic zones, makes this type of lake very appealing as a possible environment for the deposition of the banded iron formations.

THE CHEMISTRY OF DIMICTIC AND MONOMICTIC LAKES

When the water of a lake is isothermal and complete circulation is in progress the water is more or less thoroughly mixed and attains nearly the same properties throughout the entire column. Oxygen is brought down from the upper zone, and oxidizing conditions exist throughout the basin. When the water is stratified, especially during a summer stable period, oxygen tends to be consumed in the lower zone by respiration of organisms and by the oxidation of organic matter, and reducing conditions may result. Along with the oxidation-reduction potential, other factors such as the pH may vary considerably in the lower zone of the lake.

Because the dimictic lakes of the North Temperate Zone have been studied in greater detail, the chemistry of lake waters which is summarized in the following paragraphs is based mainly on that type of lake. The information relating to the summer stable period and to the autumn and spring periods of overturn in dimictic lakes is generally applicable to monomictic lakes, in which a winter stable period is absent.

The solution and precipitation of iron in lake waters is influenced strongly by both the oxidation-reduction potential and the

pH of the water; therefore, the variations in both oxygen and carbon dioxide are of importance.

Oxygen and carbon dioxide are both absorbed directly from the atmosphere, and also are obtained in other ways, principally through organic activity. Lake waters, when they are in equilibrium with the gases of the atmosphere, generally are saturated with oxygen and carbon dioxide during the periods of overturn. During the summer, when the surface zone is warmer, the solubility of gases in that zone is markedly decreased. If no other factors were involved, the oxygen and carbon dioxide concentration curves would be essentially the reverse of the temperature curve, with low concentrations in the upper, warmer waters, and higher concentrations below. Actually, however, this distribution of oxygen is only rarely encountered. Much more common is an oxygen curve which parallels the temperature trace, and shows saturation or super-saturation in the upper layer and a decrease, in some places to zero, in the bottom water zone.

Photosynthesis, by living plants, involves the use of carbon dioxide and the production of oxygen, while respiration produces carbon dioxide. In a 24-hour period there is a net production of oxygen in the upper, well-lighted zone. Deeper in the water, where less light penetrates, there is a level below which there is a net production of carbon dioxide. This level is the boundary between the "trophogenic" (or upper), and the "tropholytic" (or lower) zones. In general, the trophogenic zone is approximately coexistent with the epilimnion and the tropholytic zone is approximately coexistent with the hypolimnion. In the tropholytic zone there is a difference in behaviour in different lakes, depending on the total calcium content of the lake water. Before going into this, it is necessary to review the distribution of carbon dioxide throughout the column of water.

Carbon dioxide is absorbed directly from the atmosphere by lake water, but a more important source involves the mechanism of rain water, which brings some CO_2 from the air, then acquires more CO_2 from air trapped in humus in the soil, and then dissolves calcium from the soils and rocks of the watershed, mainly as calcium bicarbonate in the presence of carbonic acid. The bicarbonate content of the water flowing into a lake is thus dependent on both the carbon dioxide content of the water and on the calcium content of the earth in the watershed. Some areas of igneous rocks may yield more calcium than areas of limestone rocks. For example, in the northern approaches to the Alps the springs coming from lime-poor but impermeable soils are actually richer in lime than those coming from the limestone rocks of the mountains, where the rain water passes through the permeable rock rapidly and has little opportunity of being charged with CO_2 in the upper layers of the soil (Ruttner, 1953, p. 57).

As is well-known, a solution of calcium bicarbonate is a complicated system with free carbon dioxide, carbonic acid which is partially dissociated, dissociated calcium bicarbonate, and hydroxide ions resulting from hydrolysis. The solution is weakly alkaline in reaction.

It has been found that many aquatic plants, in their photosynthetic activity, can take up both free CO_2 and HCO_3^- ions from the dissociation of calcium bicarbonate and substitute OH^- ions for these. A pH as high as 11 can be produced by this process, in shallow embayments with abundant vegetation. In larger bodies of water the breakdown of bicarbonate does not go so far because the water mass is too great in relation to the assimilating plant material, and there is continual mixing of surface water throughout the epilimnion. The pH of surface waters of a typical large lake in the Temperate Zone is between 8 and 9 in the summer.

The surface waters of many lakes are impoverished in CO_2 during the summer, as a result of photosynthetic activity, and in calcium-rich lakes there is a precipitation of considerable amounts of calcium carbonate.

Referring back to the "tropholytic" zone, the lower layer of water in which there is a net production of carbon dioxide, there is an increase in the carbon dioxide content of the water in a lake which is low in calcium and therefore a lowering of the pH. In such lakes, the hypolimnion may become acidic during the summer.

In contrast, in a lake which is high in calcium the calcium carbonate precipitate produced in the epilimnion settles into the

hypolimnion, reacts with the free CO_2 there, and thus maintains a *relatively* high pH.

The total organic productivity of a lake has a very important effect on the chemical environment and on the nature of the sediments deposited. Lakes are broadly classified into two distinct types: *eutrophic* and *oligotrophic*.

Eutrophic lakes are high in nutrients and thus have a relatively large crop of organisms. Oxygen production in the well-lighted epilimnion is high. Deeper in the lake, however, any living organisms present use up the oxygen, and the large quantity of dead organic matter settling from the upper levels consumes a large amount of oxygen during its decomposition. The extent of the oxygen deficiency in the hypolimnion of a temperate-zone lake is a fairly accurate measure of the productivity of the lake. Reducing conditions exist in the hypolimnion of most eutrophic lakes.

Oligotrophic lakes, which are low in nutrients, have a relatively small organic productivity, and therefore there is less consumption of oxygen in the hypolimnion. The waters of this lower zone may retain a small amount of free oxygen throughout the summer stagnant period.

From this brief review, it may be seen that several variations of the fresh-water environment occur. All of these are well-documented by limnological studies.

IRON

Iron appears as a dissolved component in natural waters only under special circumstances. The reason for this lies in its peculiar solubility relations and in particular because it can be either bi- or tri-valent as the ferrous or ferric form. In general, iron in the ferric form is highly insoluble, while in the ferrous form it may be highly soluble. Cooper (1937) has shown that iron under reducing conditions, at a pH of 6, is 100,000 times more soluble than it is under oxidizing conditions, at a pH of 8.5.

Numerous studies of lakes in the Temperate Zone have shown that during the period of summer stability, when the oxygen content of the hypolimnion water sinks *nearly* to zero, or lower, all of the conditions necessary for the reduction of iron are present. In a lake of moderate to high organic productivity iron is reduced in the suspended particles settling from above, and also in the bottom sediments, and it goes into solution in several possible forms; ferrous bicarbonate, sulfate, or ferrous-organic compounds. Throughout the duration of the summer stable period the iron content of the hypolimnion increases and reaches relatively high values. Solution, rather than deposition, is the rule.

As soon as circulation begins in the autumn and oxygen is brought to the depths, the iron is oxidized and ferric compounds must be precipitated. Only a small amount of oxygen is needed. The precipitate, such as ferric hydroxide, can subside to the bottom before it is caught up by the circulation and transferred to the upper levels in suspension. Thus there need be no significant loss of iron through the lake's outlet, and the total iron content of the lake will be sedimented on the lake bottom. The hypolimnion of a eutrophic lake thus operates as a trap for iron. As soon as the next stagnation period begins and oxygen disappears from the bottom waters, the conditions for reduction to the ferrous state arise again at the boundary of the bottom ooze, and at least a part of the precipitated iron may go into solution. The greatest amount of iron is sedimented during the circulation periods.

If the lower water contains hydrogen sulfide, a precipitation of ferrous sulfide can take place when the waters are alkaline. At lower pH, the ferrous sulfide is more soluble. The content of H_2S in open lake waters generally is zero or negligible, however, and a complete precipitation of iron through the agency of sulfide formation can scarcely occur. In most lakes, if iron sulfide occurs in the bottom sediment the iron probably was deposited in the ferric form during the periods of overturn and was later reduced and combined as a sulfide within the bottom sediment.

The foregoing paragraphs discussing iron in lakes are based on Ruttner (1953, p. 74–79), and on Hutchinson (1957, p. 691–726).

In summary of the foregoing discussion of iron in the fresh-water environment, it may be said that iron is not deposited, but tends to dissolve and remain in the water of the hypolimnion, during the summer season. This is especially true in a lake with a low calcium content and a relatively low pH in the hypolimnion. Iron is precipitated

in the ferric state and settles to the bottom during the periods of overturn. In a monomictic (sub-tropical to warm-temperate zone) lake there would be a simple alternation between a period of precipitation of iron, in the winter, and one of non-precipitation in the summer. The particular iron mineral which is formed depends on the pH and Eh of the environment, as shown by Krumbein and Garrels (1953) and by Huber (1958). The stability fields of hematite, magnetite, siderite, and pyrite all include the ranges of pH and Eh which occur in natural lake environments.

SILICA

The solution and precipitation of silica in the sedimentary environment is not well understood, and contradictory statements may be found in the recent literature on the subject.

If we may resort to the precipitation of silica by *organisms* in order to explain the silica layers which are interbedded with iron, there is no difficulty. Ruttner, in Fundamentals of Limnology (1953), makes the following statements: "A major decrease in dissolved silica is regularly found in the epilimnion of lakes after a bloom of diatoms" (p. 83), and "In contrast to that of lime and iron, the precipitation of silicic acid from water always occurs firmly bound to living cells. It is well-known that the diatoms, whose siliceous shells in sinking to the bottom enrich the ooze with SiO_2, are most important in this process, but under certain conditions the siliceous cysts of the flagellate group. . . play a role that is not to be underestimated. The greatest quantities of diatoms are sedimented from the plankton of the pelagial region. For this reason the deep water sediments on the whole are richer in SiO_2 than the littoral. In lakes . . . in which allochthonous sediments are negligible, there remains after the destruction of the organic portion of the diatoms a more or less pure siliceous deposit . . . " (p. 168).

This mechanism, if it existed in Precambrian fresh-water basins, would be quite adequate to account for deposition of silica during various seasons, and it would thus give layers of silica which alternated with the layers of iron deposited during the cold-season overturn.

However, because there is no trace of an organic origin of the Precambrian silica bands, it is desirable to investigate the possibility of inorganic precipitation of the silica.

Our knowledge of the behaviour of silica in the sedimentary environment is very inadequate. The question of the origin of cherts is still not answered to the satisfaction of most geologists. Some cherts are definitely secondary, and others originated as primary deposits precipitated by organisms. The question still remains as to whether some siliceous deposits are primary inorganic precipitates. Some writers favor this interpretation, for some deposits.

The form in which silica occurs in water was assumed to be the colloidal state, by practically all investigators until very recently. However, Alexander, Heston, and Iler, in 1954, stated that a molybdate color test, which is rapid for simple silicic acid proves that silica is present in water in true solution, as H_4SiO_4.

Correns, in 1949 (p. 210), indicated that the solubility of silica decreased slowly with decrease in pH from 11 to about 6.5, and that the solubility decreased more rapidly in the range from pH 6.5 to 4.5 (his graph of those relationships is reproduced on p. 160 of Mason, 1958). Correns, in 1950 (p. 51), showed a slow decrease in solubility of silica from pH 9 to pH 6, and a more rapid decrease from pH 6 to pH 5.

Iler (1955, p. 45), reports that solutions of silicic acid or colloidal silica usually gel most rapidly within the range of pH 5 to 7. He shows a curve which is based on experimental work by several investigators. He states further that the same conditions which promote gelling of the silica also promote the polymerization of silica to form precipitates.

Because a pH in the range of 5 to 7 is possible in the hypolimnion of a calcium-poor lake with low or moderate organic productivity, the data of Correns and of Iler suggest that precipitation of silica may occur in such an environment.

Krauskopf (1956, p. 4), however, in reviewing the work of others, states that the work by Alexander, Heston, and Iler (1954) indicates that the solubility of amorphous silica is at least as great in acid as in dilute alkali, and Krauskopf's own conclusion was

that the solubility of amorphous silica is little affected by changes of pH in the range 0–9, but increases rapidly as the pH rises above 9.

The disagreement indicated in the foregoing paragraph can not be resolved in the present paper.

Siever (1957, p. 838–839) has suggested that inorganic precipitation of silica in surface waters may have been a common occurrence in earlier geologic time: "We may ask whether the silica cycle, at least that part of it involved in the sedimentary cycle, operated in the same way throughout the known history of the earth. . . [In the Precambrian] the concentration of silica in surface waters may have been quite different from today. . . . We can suppose that the extensive weathering of silicate rocks by rain waters with an amount of CO_2 dissolved somewhat higher than at present (Rubey, 1951, p. 1124) would contribute much more silica to solution . . . than at present. At the same time there may have been no large population of silica-secreting organisms that would biochemically precipitate silica and maintain low concentrations of silica in the oceans. . . . The diatoms and radiolaria had not yet evolved, and it is uncertain how early the siliceous sponges developed. Hence, . . . we may postulate a primitive ocean that was saturated with $Si(OH)_4$. . . . As additional silica was added, amorphous silica must have started to precipitate inorganically." The same statements could be made in regard to precipitation of silica in lake waters, because there is little effect of ionic strength of aqueous solutions on the the solubility of amorphous silica, in the range of concentrations occurring in fresh water and sea water (Krauskopf, 1936).

A possibility which should not be overlooked is that silica may have been deposited at a more or less constant rate throughout the year; and that the iron, being deposited only during the winter, so diluted the silica deposit of that season as to give an alternation between silica layers (summer deposit) and iron-rich,silica-poor layers (winter deposit).[2] However, if the silica were precipitated inorganically from saturated solutions, and if the delivery of silica from the source areas were limited mainly to the summer season (as proposed by Alexandrov, 1955), silica would have been deposited mainly during the warmer part of the year.

[2] The writer is indebted to Dr. Robert M. Garrels of Harvard University for suggesting this possibility (personal communication, July, 1958).

BANDED DEPOSITS OF THE GREAT LAKES

Rhythmic deposition of iron, in small quantitites, is well shown by deep-water sediments of the Great Lakes of North America. Kindle (1925, p. 48) described a core sample, 3½ feet long, from a depth of 615 feet in Lake Ontario, as composed of uniformly fine-textured ooze throughout and with alternating bands of black and buffish-gray color. The black bands range from "the thickness of a sheet of coarse paper to ⅛ of an inch or a little more. The gray buffish bands between these vary from $\frac{1}{16}$ to 1 inch in thickness. . . . When dry the colour is a uniform ash grey. The banding disappears after a half hour's exposure to the air. . . . Diatoms are common throughout the sample."

The writer has found similar banded sediment in the deep water of Lake Michigan (as reported briefly in Hough, 1958, p. 73), and in the deep water of Lake Huron. The upper several feet of clay are essentially homogeneous in texture but contain thin jet-black bands which range from a fraction of a millimeter to about 6 mm in thickness and are separated by gray bands which generally are slightly thicker. Differential thermal analysis of the black material, while it was still fresh, showed no organic matter but an exothermic reaction at about 450° C indicated the presence of iron sulfide. X-ray analysis showed that hematite appeared when the black-band material faded to a yellowish-gray color. In some of the core samples from Lakes Michigan and Huron the black-banded dark gray clay is overlain by several centimeters of rusty-brown banded yellowish-buff clay. The writer believes that the iron is deposited in the oxidized state and that reduction takes place after burial.

The amount of iron in the Great Lakes deep-water sediments is very small, and these sediments cannot be considered as iron formations. The banding of the sediments, however, does illustrate the rhythmic precipitation of iron in a fresh-water environment. In the Great Lakes the

amounts of iron and silica in the lake waters are very slight. The concentration of silica averages about 2 parts per million (Ayers and others, 1956, 1958).

PROPOSED ENVIRONMENT OF DEPOSITION OF PRECAMBRIAN BANDED IRON FORMATIONS

The present writer proposes the following specific conditions to account for deposition of the middle "Huronian" type of banded silica and iron formations.

(1) *The typical sequence of quartzite-slate-banded silica and iron formation was deposited in a region of very mature geomorphic development.* The clastic components of the sequence, quartz sand and clay, are typical products of a mature terrane. Weathering had already removed most of the oxides of calcium, sodium, magnesium and potassium from this terrane, but the less mobile oxides of silicon and iron remained to be delivered to the basin of deposition. Where the quartzite-slate-chemical sediments are in sequence, they appear to record a progression, late in a geomorphic cycle, from deposition of coarser-grained mature clastic sediments, to finer-grained clastic sediments, to chemical sediments essentially devoid of clastics. During deposition of this sequence, depth of water in the basin increased. If the quartzite, slate, and chemical sediments are in part time-equivalents, as suggested by Tyler and Twenhofel, they still may be considered as deposits in a region of very mature geomorphic development.

(2) *The climate of the region was subtropical to warm-temperate, with moderate to high rainfall.* This climate resulted in the leaching of silica from the soils during the hotter part of the year, and of iron from the soils during the colder part of the year, as proposed and described in detail by Alexandrov (1955). The seasonal delivery, alternately, of silica and of iron to the basin of deposition is not here considered to be a primary cause of the banding of the iron formations, but it coincided with the periods of deposition of those materials as controlled by processes in the basin of deposition.

(3a) *The environment of deposition was a fresh-water lake, of sufficient depth to permit development of density stratification of the water in the summer and of sufficient area to insure good development of a typical annual cycle.* It had no connection with the sea, except for an outlet channel which permitted discharge but did not permit return flow from the sea. The presence of such a large fresh-water lake in a geomorphologically mature region is considered as an improbable occurrence that, statistically, would be expected to happen only infrequently.

(3b) *The annual cycle of the lake was of the monomictic type, with one period of stable density stratification in summer alternating with one period of complete circulation in winter.* This monomictic pattern is typical of sub-tropical and warm temperate climatic zones. During the summer the warmer upper layer of water, the epilimnion, remained well-mixed, was saturated with oxygen, and had a relatively high pH, probably between 8 and 9. The colder lower layer of water, the hypolimnion, was isolated from the atmosphere and tended to develop an oxygen deficiency. During the winter the entire column of water had a temperature near the temperature of maximum density, and was well-mixed. It was saturated with oxygen and had a relatively high pH.

(4) *The basin of deposition had a moderately low organic productivity, owing to low concentrations of nutrients.* This was determined by its occurrence in a region of mature geomorphic development, from which most of the available calcium, sodium, magnesium, potassium, and other more soluble materials had already been removed. As a consequence of the limited productivity the lower layer of water in the summer developed only a moderate oxygen deficiency which resulted in a moderate lowering of Eh of the water.

(5) *In summer the lower layer of water, the hypolimnion, had a relatively low pH because of a net production of carbon dioxide and a low calcium content.* Because of the relatively low organic productivity, the net production of carbon dioxide was not large. The lowering of pH during the summer was, therefore, moderate, to between 5 and 7.

Under the conditions outlined in the foregoing numbered paragraphs there would be a minimum of clastic sedimentation and the principal inorganic substances delivered to the basin of deposition in solution or in colloidal suspension would be iron and silica. Most of the more mobile oxides already

would have been removed from the source area, and alumina, considered by several investigators to be less mobile than silica and iron (Steidtmen, 1908, p. 406; Leith and Mead, 1915, p. 16; Correns, 1949, p. 210; Pettijohn, 1957, p. 509), would have tended to remain in the source area, or possibly to have been transported as a component of clays.

The amounts of iron and silica removed from the source area by weathering, under annual fluctuations of conditions in a sub-tropical or warm-temperate climate with moderate to high rainfall, would have been adequate to account for the volumes of iron and silica in the banded iron formations.

In the environment of deposition which has been proposed, a fresh-water lake relatively low in nutrients (especially in calcium) and existing in a sub-tropical or warm-temperate zone, iron and silica would be deposited as follows. During the summer, in the epilimnion of the lake, iron would be oxidized and would precipitate, but on settling into the hypolimnion it would be reduced and would go into solution; no deposition would occur. During the winter, when the water was uniformly cold and undergoing complete circulation, the iron would be oxidized to the ferric state throughout the lake and would precipitate, settling to the bottom. The largest amount of iron probably would be deposited during a relatively brief period at the beginning of the cold-season, when the summer's accumulation of iron in solution in the hypolimnion was first exposed to oxygen-saturated water at the onset of complete circulation. Silica possibly was deposited by the agency of organisms, but more probably by direct inorganic precipitation. If, by either process, the silica were deposited more or less constantly throughout the year it would appear in the deposit as bands separated by iron-rich, silica-poor bands of iron mineral. More silica may have been deposited during the warm part of the year because of the delivery of greater quantities of silica to the basin of deposition in that season, and also possibly because of a slightly lesser solubility of silica in the hypolimnion waters of the summer season.

The particular iron mineral which would form would depend on the particular combination of pH and Eh of the environment. The fields of stability of the common iron minerals occurring in the banded silica and iron formations, namely hematite, siderite and magnetite, all include pH and Eh values which are attainable in the fresh-water environment which has been described.

The question immediately may be raised, why are there no deposits of banded silica and iron in the rocks younger than the "Huronian"? The writer suggests that the particular combination of factors required by his hypothesis has not been repeated in later geologic time. Long-continued erosion tends to destroy lakes, and the presence of large and deep lakes in a very maturely weathered and eroded terrane is unlikely. Both the source area and the basin of deposition are required to be in a sub-tropical to warm-temperate climate. Further, there may have been a tendency toward greater concentration of silica in surface waters in Precambrian times because of a slightly higher carbon dioxide content of the atmosphere, as suggested by Siever (page 427).

The hypothesis described here is intended to apply only to the typical banded silica and iron formations, in which the iron minerals are dominantly hematite, siderite, or magnetite. Some of the iron silicates, where they are included in the banded iron formations, and small amounts of pyrite, may possibly be included as deposits in a lucustrine environment. Deposits of calcium and magnesium carbonate and large quantities of pyrite are almost certainly of marine origin and these specifically are excluded from the present hypothesis.

REFERENCES

ALEXANDER, G. B., HESTON, W. M., AND ILER, R. K., 1954, The solubility of amorphous silica in water: Jour. Phys. Chemistry, v. 58, p. 453–455.

ALEXANDROV, E. A., 1955, Contribution to studies of origin of Precambrian banded iron ores: Econ. Geology, v. 50, p. 459–468.

AYERS, J. C., ANDERSON, D. V., CHANDLER, D. C., AND LAUFF, G. H., 1956, Currents and water masses of Lake Huron: Univ. of Michigan Great Lakes Res. Inst. Tech. Paper 1. 101 p.+Append.

AYERS, J. C., CHANDLER, D. C., LAUFF, G. H., POWERS, C. F., AND HENSON, E. B., 1958, Currents and water masses of Lake Michigan: Univ. of Michigan Great Lakes Res. Inst. Tech. Paper 3. 169 p.

COOPER, L. H. N., 1937, Some conditions governing the solubility of iron: Proc. Royal Soc. (London) B 124, p. 229–307.
CORRENS, C. W., 1949, Einführung in die Mineralogie. Springer-Verlag, Berlin, 414 p.
———, 1950, Zur Geochemie der Diagenese: Geochim. et Cosmochim. Acta, v. 1, p. 49–54.
GOODWIN, A. M., 1956, Facies relations in the Gunflint Iron Formation: Econ. Geology, v. 51, p. 565–595.
GRUNER, J. W., 1922, Organic matter and the origin of the Biwabik iron-bearing formation of the Mesabi range: Econ. Geology, v. 17, p. 407–460.
HOUGH, J. L., 1958, Geology of the Great Lakes. University of Illinois Press, Urbana, 313 p.
HUBER, N. K., 1958, The environmental control of sedimentary iron minerals: Econ. Geology, v. 53, p. 123–140.
HUTCHINSON, G. E., 1957, A treatise on limnology v. 1, John Wiley and Sons, Inc., New York, 1015 p.
ILER, R. K., 1955, Colloid chemistry of silica and silicates. Cornell Univ. Press, Ithaca, 324 p.
JAMES, H. L., 1954, Sedimentary facies of iron-mineral formation: Econ. Geology, v. 49, p. 235–293.
KINDLE, E. M., 1925, The bottom deposits of Lake Ontario: Royal Soc. Canada Trans., 3rd ser., v. 19, p. 17–72.
KRAUSKOPF, K. B., 1956, Dissolution and precipitation of silica at low temperatures: Geochim. et Cosmochim. Acta, v. 10, p. 1–26.
KRUMBEIN, W. C., AND GARRELS, R. M., 1952, Origin and classification of chemical sediments in terms of pH and oxidation-reduction potentials: Jour. Geology, v. 60, p. 1–33.
LEITH, C. K., 1934, The pre-Cambrian: Geol. Soc. America Proc. 1933, p. 151–180.
LEITH, C. K., AND MEAD, W. J., 1915, Metamorphic geology. Henry Holt and Company, New York.
MASON, B., 1958, Principles of geochemistry. 2nd ed., John Wiley and Sons, Inc., New York, 310 p.
MOORE, E. S., AND MAYNARD, J. E., 1929, Solution, transportation and precipitation of iron and silica: Econ. Geology, v. 24, p. 272–303, 365–402, 506–627.
OFTEDAHL, C., 1958, A theory of exhalative-sedimentary ores: Geologiska. Föreningens I Stockholm Förhandlinger, Bd. 80, H. 1, p. 1–19.
PETTIJOHN, F. J., 1957. Sedimentary rocks. 2nd ed., Harper and Brothers, New York, 718 p.
RUBEY, W. W., 1951, Geologic history of sea water: Geol. Soc. America Bull., v. 62, p. 1111–1147.
RUTTNER, F., 1953, Fundamentals of limnology. Transl. by Frey, D. G., and Fry, F. E. J., University of Toronto Press, Toronto, 242 p.
SAKAMOTO, T., 1950, The origin of the pre-Cambrian banded iron ores: Am. Jour. Sci., v. 248, p. 449–474.
SIEVER, R., 1957, The silica budget in the sedimentary cycle: Am. Mineralogist, v. 42, p. 821–841.
STEIDTMAN, E., 1908, A graphic comparison of the alteration of rocks by weathering with their alteration by hot solutions: Econ. Geology, v. 3, p. 381–409.
TYLER, S. A., AND TWENHOFEL, W. H., 1952, Sedimentation and stratigraphy of the Huronian of Upper Michigan: Am. Jour. Sci., v. 250, p. 1–27, 118–151.
VAN HISE, C. R., AND LEITH, C. K., 1911, The geology of the Lake Superior region: U. S. Geol. Survey Mono. 52, 641 p.
WELCH, P. S., 1935, Limnology. McGraw-Hill Book Company, Inc., New York, 471 p.
WOOLNOUGH, W. G., 1941, Origin of banded iron deposits—a suggestion: Econ. Geology, v. 36, p. 465–489.

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FIGS. 1–6, DECEMBER, 1958

OCCURRENCE OF ALKALI METALS IN SOME GULF OF MEXICO SEDIMENTS[1]

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ABSTRACT

The abundance of the alkali metals in 130 samples from the Gulf of Mexico was determined spectrographically. The results show that only a slight enrichment of rubidium with respect to potassium exists in the sediments while there is present a significant enrichment of cesium with respect to both potassium and rubidium. The potassium-sodium ratios indicate that these two elements are present in about the same proportions as in igneous rocks. The lithium abundance is similar to that found in igneous rocks.

Thermal analyses suggest that rubidium is enriched with respect to postassium in the illite-rich sediments and that these sediments are relatively low in cesium. That a relatively high lithium content is associated with montmorillonite-rich sediments is also suggested.

The alkali metal content of the sediments apparently does not vary systematically with depth below the present sedimentary interface or with distance from shore. In the sediments from the eastern part of the Gulf the distribution of all the alkali metals is similar.

The results of the investigation suggest that much of the separation of the alkali metals and the enrichment of one with respect to another may occur during weathering and that the hydrated radii and ionic potential based on the hydrated radii are not the only factors which control the behavior of the alkali metals during the weathering and sedimentary cycles.

INTRODUCTION

Purpose of Investigation

While the alkali metal content of sedimentary rocks is generally well-known, particularly for sodium and potassium, relatively few analyses are available for sediments from the present oceanic areas. Our knowledge of the amounts of sodium and potassium present in sediments of all ages is moderately extensive, but it is limited in the case of the other alkali metals: lithium, rubidium, and cesium. To quote Rankama and Sahama (1949), "The number of analyses [of rubidium and cesium] is still deplorably small."

Canney (1952) and Goldschmidt, Bauer, and Witte (1934) investigated the distribution of cesium and rubidium in sediments underlying present land areas. To the best of the author's knowledge no analyses of rubidium or cesium have been reported for sediments forming currently on the bottoms of the oceanic areas. The availability of samples from several environments of deposition make possible the comparison of the alkali metal content of sediments from the various environments.

Although the absolute occurrences of rubidium and cesium in sediments and sedimentary rocks are interesting in themselves, a complete understanding of the geochemistry of these elements necessitates a study of the potassium and sodium in the same materials. Thus the occurrence of the entire alkali metal group is reported upon.

Materials Used

The majority of samples were obtained from cores taken in the western part of the Gulf of Mexico and from cores taken in the eastern part of the Gulf during cruises of the *Atlantis* from the Woods Hole Oceanographic Institution in 1947 and 1951 respectively. The first cruise was sponsored jointly by Woods Hole and the Geological Society of America (Stetson, 1949, 1953); the second was sponsored by Woods Hole. All of the coring on these two expeditions was outside the ten fathom line. The physical nature of some of the sediments has been recently described by Greenman and Le Blanc (1956).

The cores were sampled at the top, or as close to the top as possible, at approximately 75 cm, and approximately 150 cm from the

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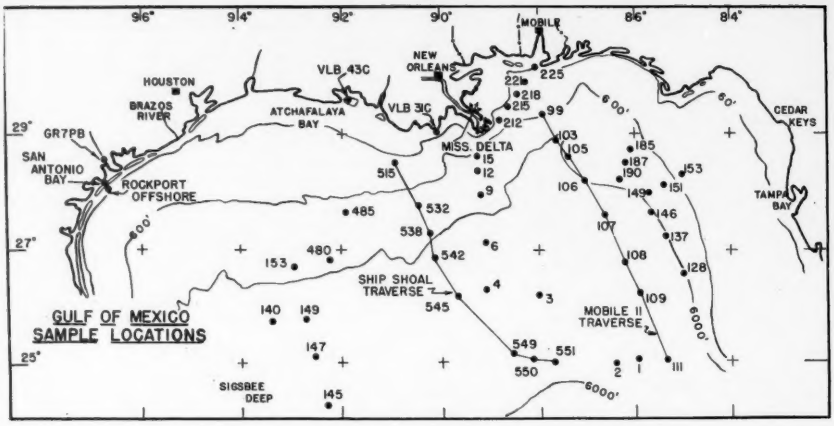

FIG. 1.—Outline map of the Gulf of Mexico showing sample locations.

top. Compaction during coring operations and shrinkage with the drying of the sediments make these depths only approximate.

Some of the samples were obtained from short cores (about 18 inches in length) which were taken primarily for the study of the foraminiferal content of the upper layers of the sediment on the bottom of the Gulf (Stetson, 1953, p. 6). Prior to the sampling by the author the upper two inches of the material had been removed from these short cores for study of the foraminiferal content. However, the material in each individual core seemed to be more or less uniform, and therefore it is believed that the sediments from these cores are representative of the material forming presently at the surface.

A number of samples from within the ten fathom line were used. Some of these came from the east side of the Mississippi Delta; others came from the area of Atchafalaya Bay. Samples were obtained from San Antonio Bay near Rockport, Texas, and also offshore in the same area. For comparison purposes seven composite samples were used. Figure 1 shows the locations of the various samples.

ANALYTICAL PROCEDURES

The emission spectrographic method using a D.C. arc provides a rapid, reasonably accurate method for accumulating in a relatively short time a large amount of data on the abundance of elements in rocks and soils, particularly where the abundances of the elements are so small that the element cannot be detected by wet chemical methods. This was the method used in the investigation. The theory underlying the use of the spectrographic techniques is treated adequately in many reference books and need not be considered here. (See Ahrens, 1950, for bibliography.)

The following lines were used: Na_{5688}, K_{6938}, Rb_{7947}, Li_{8126}, and Cs_{8521}. Except for cesium, all of the elements were detectable using the lines indicated. In the case of cesium, the detection limit for the procedures used appeared to be of the order of 0.0003% Cs_2O, although no check was made to determine the limit precisely.

A total energy method with cathode excitation was utilized in the study. Since the alkali metals all distill off in the early part of the burn, it is possible to stop the arcing before the sample has been completely consumed.

The conditions under which the materials were arced were basically the same; however, because of the physical and chemical nature of some of the samples, it was necessary to use three types of electrodes: $\frac{1}{8}$-inch pure carbon, $\frac{1}{8}$-inch pure graphite, and $\frac{3}{16}$-inch pure graphite. The samples were run in batches of 20 to 35 with each sample being analyzed in triplicate. Each batch had a set of standards to compensate for any variations from the "standard conditions."

In the $\frac{1}{8}$-inch electrodes the sample weights varied from 6 to 11 milligrams. The $\frac{3}{16}$-inch electrodes held about 30 milligrams.

A step sector with a step height of 1.5 mm and an aperture ratio of two was employed in calibrating the plates. Seven full steps were effective. For the $\frac{1}{8}$-inch electrodes a current of three amps was used. For the $\frac{3}{16}$-inch electrodes a current of six amps was used.

Eastman-Kodak D-19 developer was used to develop the photographic plates. It was maintained at a temperature of 18° C, and the plates were left in the developer for $4\frac{1}{2}$ minutes.

Standards

A standard granite and diabase (Fairbairn and others, 1951) were used as the basic standards for the sodium, potassium and rubidium.

Mixes of the granite and diabase were prepared to serve as standards. Lithium and cesium standards were made by adding to a 1:1 mixture of the granite and diabase 0.228% Li and 0.776% Cs in the form of chemically pure Li_4SiO_4 and CsCl respectively. This basic mixture was diluted with more 1:1 mixture of granite and diabase until a set of standards was developed which ranged in lithium content from 0.0269 to 0.00388% Li_2O and in cesium content from 0.0413 to 0.00095% Cs_2O. The cesium content of the 1:1 mix was determined as 0.0001% through the use of a standard addition plot.

An additional sodium standard was prepared by mixing one part of the standard diabase with four parts of a plastic clay (U.S. Bureau of Standards No. 98) to obtain a mixture containing 0.76% Na_2O. A 1:1 mixture of the diabase and a potash feldspar (U.S. Bureau of Standards No. 70) provided a standard with 6.62% K_2O.

Sampling

The Gulf of Mexico samples were taken from the cores by the author. Because most of the material had dried and become extremely hard and tenacious, it was necessary to cut the samples out along the planes of stratification, and, depending upon the lithology, a large or small sample was obtained.

Sintering

The samples were dried at 110°C, weighed, and then sintered in an electric furnace at a temperature of 450° C for an hour in order to remove organic material which would interfere with the smooth arcing of the materials. The weight loss on ignition is shown in table 11.

F. C. Canney informed the author (oral communication, November, 1951) that he had encountered no loss of cesium or rubidium as a result of sintering sedimentary material at a 450° C. temperature. *The Handbook of Chemistry and Physics* (1945, p. 402) shows that there are no lithium compounds which boil below this temperature. Furthermore, it seems unlikely that any of the potassium and sodium compounds which are apt to be present in the material investigated will boil at the 450° C temperature. Canney (oral communication, November, 1951) found no loss of potassium on heating. Thus it seems safe to assume that the sintering process did not cause the loss of any of the elements.

Computations

Background corrections were necessary in nearly all instances. Such corrections must be made for each line because the background is not reproduced from arcing to arcing, even in the case of the same sample. Background corrections were made also for invisible background (Canney, 1952).

The Seidel function (Nachtrieb, 1950) was used in drawing the partial characteristic curves. This function facilitates the determination of low values which fall on the curved portion of the characteristic curve if the usual method of plotting of d_0/d *vs.* intensity (Ahrens, 1950) is chosen.

The slope of the working curves approached 45°, indicating that the slopes of the characteristic curves were reasonably accurate and that the background correction was essentially correct.

ACCURACY AND PRECISION OF THE METHOD

Standard Deviation

The standard deviation for each method of arcing was determined for each element. From ten to fifteen arcings were made for

TABLE 1.—*Standard Deviations*

	Na_2O	K_2O	Rb_2O	Li_2O	Cs_2O
¼ Inch Pure Carbon Electrodes					
Average of 12 Analyses WG 542-B	3.79	4.01	0.040	0.016	0.0018
Standard Deviation	± 0.32	± 0.57	± 0.0064	± 0.0014	± 0.00029
% Standard Deviation	± 8.5	±14	±16	± 8.7	±16
¼ Inch Graphite Electrodes					
Average of 17 Analyses WG 542-B	3.64	3.35	0.037	0.019	0.0013
Standard Deviation	± 0.37	± 0.47	± 0.0056	± 0.0027	± 0.00022
% Standard Deviation	±10	±14	±15	±14	±17
3/16 Inch Graphite Electrodes					
Average of 10 Analyses EG 137-A	4.3	2.87	0.037	0.019	0.0010
Standard Deviation	± 0.58	± 0.45	± 0.0049	± 0.0024	± 0.0022
% Standard Deviation	±13.5	±15.7	±13	±13	±22

each. As may be seen in table 1, standard deviations for each method are approximately the same. Only two samples were used in determining the standard deviation, but it is felt that the data obtained from them truly represent the preciseness of the method.

Accuracy

Because the accuracy of a method differs from its precision, a means of checking the accuracy of the determinations is desirable. Some thought was given to this problem, especially to the effect of compositional differences between the standards and the unknowns. Checks were made on a flame photometer against the spectrographically-determined values for several of the samples. It is believed that the spectrographically-determined values are essentially correct and that the systematic error due to compositional effects is probably within the limits of the standard deviation. Even if there is a significant systematic error, the abundance ratios are probably correct, since all the alkali metals behave similarly in the D.C. arc.

ANALYTICAL DATA

The soluble salts were not leached from the material analyzed prior to analysis for two reasons. The first is that the soluble salts are considered to be part of the sediment. Secondly, in the process of leaching the soluble salts some of the exchangeable elements might have been removed. Thus the analyses represent not only the quantity of the alkali metals in the sedimentary materials, but also the dissolved salts which remained behind when the water evaporated. (See section on the potassium-sodium ratio for further discussion of this point.)

The spectrochemical results are listed in table 11. Histograms and scatter diagrams are used to illustrate the occurrences of the various elements from environment to environment. Except for the rubidium-cesium relationships the scatter diagrams have all been prepared using the percentage of K_2O as the abcissa and the percentage of the oxide of the other element as the ordinate. This manner of drawing the diagrams was chosen because rubidium and cesium follow potassium geochemically, and because a common standard of comparison is desirable.

Average Values

The spectrochemical results have been broken down into eight parts: VLB samples, San Antonio Bay, Rockport-Offshore, GR7PB, Mississippi Delta samples, Globigerina Oozes, Gulf of Mexico samples, and Composites. Table 2 lists the averages for the elements reported as oxides in each of these environments, together with pertinent abundance ratios based upon these average percentages.

Comparison of the averages indicates that the near-shore environments of the Gulf Coast are significantly lower in sodium, potassium, and rubidium compared to the sediments from the Gulf of Mexico proper. The sample from the Guadalupe River, near Corpus Christi, has an especially low alkali metal content.

TABLE 2.—*Average values by environment*

	No. of Samples	Percent Na_2O	K_2O	Rb_2O	Cs_2O	Li_2O
VLB	12	2.09	1.82	0.026	0.00052	0.013
San Antonio Bay	4	1.24	1.92	0.025	0.0013	0.017
Rockport-Offshore	3	2.56	1.64	0.026	0.00054	0.0089
GR 7 PB	1	0.55	0.42	0.008	0.00039	0.0044
Miss. Delta	14	1.67	0.91	0.012	0.0003	0.0081
Globigerina Oozes	19	3.57	2.13	0.026	0.00093	0.013
Gulf of Mexico (exclusive of oozes)	78	3.31	2.90	0.036	0.0081	0.014
Composites	7	1.96	1.43	0.017	0.00043	0.0091

	Ratios $\frac{K_2O}{Na_2O}$	$\frac{K_2O}{Rb_2O}$	$\frac{K_2O}{Cs_2O}$	$\frac{Rb_2O}{Cs_2O}$
VLB	0.87	70	3500	50
San Antonio Bay	1.55	76	1480	19
Rockport-Offshore	0.64	63	3200	48
GR 7 PB	0.76	53	1080	20
Miss. Delta	0.54	76	3040	40
Globigerina Oozes	0.60	82	2290	28
Gulf of Mexico (exclusive of oozes)	0.88	80	3580	44
Composites	0.73	84	3330	40

Gulf of Mexico Samples, exclusive of Globigerina Oozes

Examination of the histograms in figure 2 indicates that the bulk of the sodium and potassium contents are distributed over several percentage classes. The rubidium and lithium histograms show that each of these elements is concentrated in one percent class. Almost 50 percent of the samples have their rubidium content concentrated within the 0.035–0.040 percent Rb_2O class while almost 30 percent of the lithium content is concentrated within the 0.014–0.016 percent Li_2O class. The histogram of the cesium content indicates that 40 percent of the samples contain between 0.0006 and 0.0010 percent Cs_2O.

Histograms have also been prepared for the potassium-rubidium, potassium-cesium, potasssium-sodium, and rubidium-cesium ratios (fig. 3). The histograms for the potassium-sodium and for the potassium-rubidium ratios show definite peaks. The former is in the 0.80–0.90 class, and the

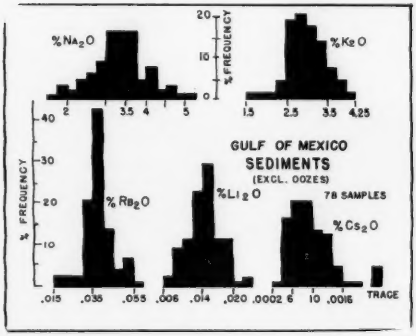

FIG. 2.—Histograms of oxide percentages, Gulf of Mexico sediments exclusive of oozes.

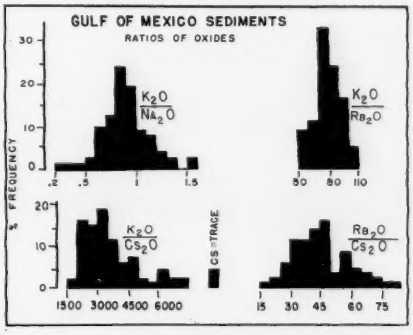

FIG. 3.—Histograms of oxide ratios, Gulf of Mexico sediments exclusive of oozes.

latter is in the 70–80 class. The potassium-cesium ratios appear to be concentrated in the 3000–3500 class, although the distribution seems to be somewhat irregular and asymmetrical toward the higher values. The rubidium-cesium ratios exhibit a moderately wide range of distribution with the main concentration of the ratios in the 45–50 class. The asymmetric distribution seen in this histogram as well as in the potassium-cesium histogram suggests that perhaps the cesium is concentrating in the sediments with relation to the rubidium and potassium. The higher values approach the ratios of the elements in igneous rocks.

Scatter diagrams for the various elements indicate that there is a general correlation between the potassium and the sodium of the samples, a good correlation between the potassium and rubidium, a moderately good correlation between the potassium and cesium, and a good correlation between the rubidium and cesium. There is no correlation between the lithium and either the sodium or the potassium. It has been found through experience (Rankama and Sahama, 1949) that lithium follows magnesium in the weathering cycle; hence it is not surprising to find a lack of correlation of lithium with the other alkali metals.

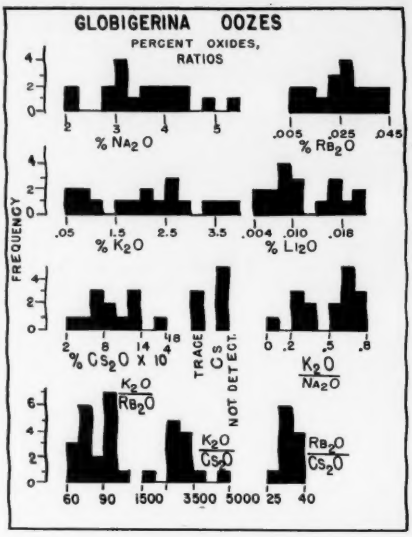

FIG. 4.—Histograms of oxide percentages and ratios for globigerina oozes.

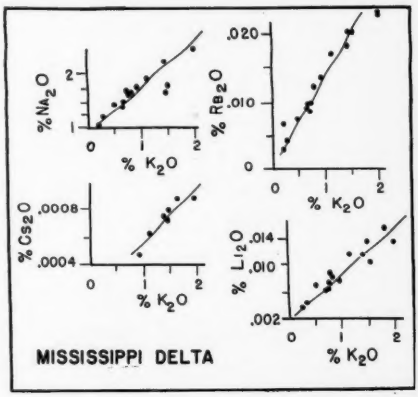

FIG. 5.—Scatter diagrams for VLB, Rockport, San Antonio Bay, and composite samples.

Globigerina Oozes

The histograms (fig. 4) for the globigerina oozes indicate a rather wide range of alkali metal content in the 19 samples recognized as globigerina oozes. The main mode of the potassium-sodium ratio is in the 0.60–0.70 class while the potassium-rubidium ratios are concentrated dominantly between 70 and 100. Those oozes containing cesium in measurable concentrations have potassium-cesium ratios which vary from 2500 to 3500. The rubidium-cesium ratios in the same samples vary from 26 to 64 with the main concentration of values being between 30 and 35.

Mississippi Delta Samples

Because of the relatively small number of samples used from this environment, scatter diagrams are utilized to illustrate the relations (fig. 5). The correlation between the potassium and the other four alkali metal elements is relatively good. Study of the diagrams indicates that a concentration of potassium between 0.25 and 1.0 percent K_2O exists in these samples while the rubidium content is concentrated dominantly between 0.008 and 0.010 percent Rb_2O. The bulk of the samples contain cesium in non-detectable or trace quantities. The lithium content is widely scattered, although there

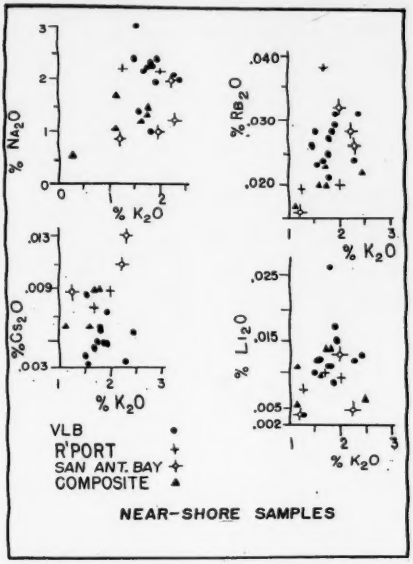

FIG. 6.—Scatter diagrams for Mississippi Delta samples.

seems to be a particular concentration within the 0.006 to 0.008 percent Li_2O range. Sodium is concentrated within the 1.25–2.0 range, with a particular concentration between 1.50 and 1.75 percent Na_2O.

The San Antonio Bay, Rockport-Offshore, and VLB Samples

The data for the alkali metal content of the samples from these three areas have been combined into one series of scatter diagrams (fig. 6) with the data from each area being indicated by the different symbols.

Comparison of the scatter diagrams for the VLB and San Antonio Bay samples with the scatter diagrams for the Mississippi Delta samples indicates that there is a lesser degree of correlation between the sodium and the potassium in the former than in the latter. The Rockport-Offshore ratios show extreme variance.

Correlation between the potassium and rubidium of the VLB samples is good while the correlation between these two elements in the San Antonio Bay samples is only fair. The potassium-cesium scatter diagram shows that the potassium and cesium contents of the VLB samples possess a moderate degree of correlation while the potassium and cesium values of the other samples are not so closely related to each other.

In the VLB samples and the San Antonio Bay samples the sodium occurs predominantly in percentages less than 2.0 percent Na_2O; the rubidium has a fairly even distribution, falling principally between 0.025 and 0.030 percent Rb_2O; potassium is concentrated between 1.5 and 2.0 percent K_2O. The sediments are low in cesium, over 40 percent containing less than 0.0006 percent Cs_2O. The lithium is concentrated between 0.010 and 0.014 percent Li_2O.

The potassium-sodium ratios center around 1.0. The potassium-rubidium ratios fall mainly between 65 and 70, although they are distributed from 50 to 95. The potassium-cesium ratios are more or less evenly distributed between 1000 and 6000. As may be deduced from the rubidium-cesium scatter diagram, the rubidium-cesium ratios in the San Antonio Bay and the VLB samples differ considerably. The average for the San Antonio Bay samples is 20 whereas the average for the VLB samples is 55.

The relations of the composite samples are also indicated in figure 6. Study of the lithium content of these samples (table 11) indicates that the Lower Eutaw and the Selma Chalk are markedly enriched in lithium compared with the rest of the composites.

VARIATIONS WITH DISTANCE FROM SHORE AND WITH DEPTH OF BURIAL

Consideration was given to possible significant abundance differences with distance from shore and with depth of burial. Two traverses were used in this study: the Ship Shoal Traverse from the western part of the Gulf and the Mobile II Traverse from the eastern part of the Gulf (fig. 1). No systematic variation in the alkali metal content with depth and/or distance from shore was detected along either of these traverses. While no definite relationship with depth is found along these two traverses, when consideration is given to all of the Gulf of Mexico samples (44 surface samples, 29 from 75 cm and 24 from 150 cm) the data seem to suggest an increase in rubidium

content in the deeper materials. There seems also to be a suggestion that the deeper sediments as a whole may contain slightly less cesium than those nearer the surface.

The Mississippi Delta samples exhibit no systematic increase with depth below the surface; just about as many increase in their alkali metal content with depth as decrease. The tendency, if any can be said to exist, is for the alkali metal content to decrease with depth in the VLB samples.

Consideration of the areal distribution of the surface samples from the eastern part of the Gulf together with their alkali metal content indicates a similar general pattern of distribution for all. The alkali metal content of the sediments increases towards the central part of the Gulf of Mexico, especially in the region of Latitude 26° N, Longitude 86° W (fig. 1). The apparent explanation of this phenomenon is the fact that the sediments west of Longitude 86° W are predominantly clay whereas those sediments occurring east of this longitude are composed predominantly of calcareous matter.

The lithium content of the sediments decreases rather sharply away from the mouth of the Mississippi River, and the decrease continues outward from the delta. An initial decrease in the alkali metal content of the samples near the delta is noted for all of the other elements, but the percentages of the elements other than lithium soon begin a general increase towards the center of the Gulf.

The nature of the potassium-rubidium ratio distribution indicates a concentration of rubidium with respect to potassium from the Mississippi River Delta toward Mobile, Alabama. Also there is a suggestion that rubidium concentrates slightly in the sediments landward from Latitude 28° N, Longitude 86° W. The deposits in this area are globigerina oozes.

CLAY MINERALS AND ALKALI METAL CONTENT

Prior to undertaking the spectrographic phase of the investigation, the author examined most of the samples with a binocular microscope in order to determine their general lithologic characteristics. The materials as a whole are so fine grained that even with use of the highest magnification available on the microscope only the partial mineral composition could be determined. Nevertheless, it was found possible to separate those samples which are composed primarily of clay minerals from those which are composed of clay- to silt-size fragments of mineral grains.

In addition to the examination with the binocular microscope some of the samples were examined with a petrographic microscope using oil immersion techniques. Differentiation between quartz and feldspar and between the various feldspars was the object of most of the petrographic work. It was found possible to accomplish this object through the proper choice of immersion oils.

Fifteen samples were analyzed with differential thermal equipment. The results are listed in table 3. The percentages of clay mineral present are probably accurate to $\pm 15\%$. Table 4 gives the samples thermally analyzed and the various ratios of the elements for each. The equipment used is not sufficiently sensitive to indicate the presence of very small percentages of either quartz or clay minerals; perhaps the minimum quantity that it will indicate is between 5 and 10% of each. However, this limitation did not affect the results of the investigation, for none of the samples contain less than 10% clay mineral. Most of the samples of high clay content probably contain a small percentage of quartz (less than 5%), but this quantity is insignificant compared to the other components.

While the data appear to be insufficient to draw any positive conclusions regarding the relationship of the alkali metals and the clay components of the sediments, it is thought that some general trends exist.

Those samples with a potassium-rubidium ratio of less than 65 are predominantly illite with the single exception of the Rockport-Offshore sample (J-35-A) which contains only about 20% clay mineral. The samples which contain illite but which possess a larger potassium-rubidium ratio all contain detrital grains of intermediate plagioclase. It is suggested that the higher potassium-rubidium ratio is related to the feldspar content and the lesser amount of clay mineral. The lower potassium-rubidium ratios probably represent a tendency for the rubidium to concentrate in illite relative to potassium.

TABLE 3.—*Results of differential thermal analyses*

Sample No.	Clay Minerals and Percent	Petrographic Description
WG 140-A	Illite (?) Low exothermic peak at 725° C.—50%	Gray clay with significant amount of undifferentiated feldspar
WG 145-B	Montmorillonite 80–90%	Light gray clay
WG 485-A	Illite—50%	Coarse, brownish gray clay; moderate amount of feldspar present
WG 538-A	Mixture of montmorillonite and illite —70%	Light gray clay; plagioclase approximately composition of andesine
WG 538-B	Illite? May be a mixture of illite and montmorillonite—60%	Gray clay about 50% of sample; some feldspar present
WG 542-A	Illite—70%	Clay minerals dominant; plagioclase of intermediate composition
WG 542-C	Illite—70–80%	Pure clay mineral; may be some carbonate present
WG 549-B	Montmorillonite and moderate portion of carbonate—30%	Whitish clay with a moderate percentage of carbonate
EG 9-A	Illite—50%	Gray clay with some feldspar and less than 5% quartz
EG 12-A	Illite—30–40%	Gray clay with less than 5% silt-size quartz grains
EG 15-A	Illite—50%	Dark gray clay; albite-oligoclase feldspar; 5% silt-size grains of quartz
EG 99-A	Mixture of montmorillonite and illite —40%	Dark gray clay with rare silt-size quartz grains; intermediate plagioclase
EG 111-B	Montmorillonite ? small amount of kaolinite—50%	Red clay with frosted quartz grains up to 0.08 mm; nonclay fraction mostly intermediate plagioclase
J 35-A	Illite—20%	Reddish buff clay; large proportion is albite-oligoclase; some quartz

The samples containing illite are as a group slightly lower in potassium than the other samples; WG 542-A is particularly low in potassium. The illite group of clay minerals is generally thought to provide the sites for fixation of potassium in the sediments. This apparent relationship between low potassium content and high illite content does not agree with our present knowledge of the chemical constitution of the illite group.

Because of the similarity of the peaks for montmorillonite and illite it is possible that the thermogram of WG 542-A was interpreted incorrectly. This sample may actually be a mixture of montmorillonite and illite. If it is a mixture, the relatively low potassium content may be accounted for.

Grim, Dietz, and Bradley (1949) have suggested that illite may be brought into the marine environment in a "degraded" form, there to be changed into "normal" illite by adsorption of potassium from sea water. The potassium is removed from the illite during the weathering processes, and the "degraded" material is transported to the oceans before it regains its potassium.

Another suggested reason for the low potassium content in WG 542-A is that the illite in this particular sample may not have adsorbed its full capacity of potassium from the sea water and that the material is thus

TABLE 4.—*Ratios for samples analyzed thermally*

Sample No.	K_2O / Na_2O	K_2O / Rb_2O	K_2O / Cs_2O	Rb_2O / Cs_2O
WG 140-A	1.01	75	2150	29
WG 145-B	1.16	100	2380	24
WG 485-A	1.03	101	2210	22
WG 538-A	0.86	77	2910	38
WG 538-B	0.71	58	2370	41
WG 542-A	0.53	59	3620	62
WG 542-C	0.92	60	2770	46
WG 549-B	0.48	82	—	—
EG 9-A	0.84	75	3390	45
EG 12-A	0.89	61	3540	58
EG 15-A	0.75	71	3050	43
EG 99-A	1.04	86	2440	39
EG 111-B	0.99	106	6320	60
J 35-A	0.51	44	2170	49

lower in potassium than the illite content would indicate.

The sodium content of the sediments shows no particular relationship with the type or the quantity of clay mineral present in a sample. The lithium content of all the samples analyzed thermally is approximately the same, although there may be a slight tendency for the lithium to concentrate in the samples containing montmorillonite and mixtures of montmorillonite with illite or kaolinite. The illite-bearing samples are as a whole lower in Cs_2O than the other samples. The potassium-cesium ratios are higher, indicating that there is less concentration of cesium in relation to the potassium in these materials than in the others. There is no definite correlation between the clay mineral and the rubidium-cesium ratios, although a tendency to higher values may possibly be indicated.

IONIC POTENTIAL AND HYDRATED RADII

For a discussion of the basic geochemical principles involved in interpreting the results of the spectrochemical analyses, the reader is referred to the work of Rankama and Sahama (1949). Here he will also find a discussion of the occurrence of the alkali metals in igneous rocks as well as a discussion of their respective geochemical cycles. However, it is believed that some note should be made here of the theoretical role of ionic potential and the hydrated radii.

TABLE 5.—*Ionic and hydrated radii*

Element	Ionic Radius (r)	Hydrated Radius (r_h) (Gedroiz)	$\frac{Z}{r}$	$\frac{Z}{r_h}$
Li	0.68	3.65	1.47	0.274
Na	0.98	2.80	1.02	0.358
K	1.33	1.90	0.752	0.526
Rb	1.47	1.80	0.680	0.555
Cs	1.67	(1.67)	0.600	0.600

In the process of weathering one of the important agents is the hydration of the minerals of the rocks and hydration of the elements which comprise the minerals. The alkali metals are among the most soluble of the elements, and being easily hydrated, they are removed early from the rock-forming minerals. Because of their relative ease of hydration, the alkali metals do not behave during the weathering and the sedimentary cycles in the manner expected from consideration of their ionic radii and ionic potential based upon their ionic radii alone.[2] If they followed the geochemical paths suggested by their ionic potentials, lithium would be relatively enriched in the sediments over the other alkalies and cesium would be a significant trace element in sea water. However, according to present knowledge, cesium is concentrated in sediments in relation to lithium. Instead of the ionic radius being the controlling factor, the hydrated radius of a given ion apparently controls the behavior of the element in the sedimentary cycle. Table 5 gives the ionic radii, the hydrated radii, and the ionic potentials based upon these radii.

Boyd and others (1947) have indicated that the hydrated radius of cesium is essentially equal to its ionic radius; hence in the table the ionic potential based on the hydrated radius is actually the ionic potential of the ion itself. It may be seen that the order of decreasing hydration is Li > Na > K > Rb > Cs and that the relative hydration decreases with increasing atomic weight.

Because of the small difference between the ionic potentials based on the hydrated

[2] Ionic potential $= Z/r$, where Z = valence and r = radius.

TABLE 6.—*Alkali metal content of sea water* (Svedrup and others, 1942)

Element	Content in Sea Water mg/kg
Li	0.1
Na	1.0×10^{4}
K	380
Rb	0.2
Cs	0.002

TABLE 7.—*Alkali metals left on evaporation of sea water (Assuming 100% water content)*

Element	Weight Percent
Li	1×10^{-5}
Na	1.07
K	0.04
Rb	2×10^{-5}
Cs	2×10^{-7}

radii, rubidium and potassium should follow one another closely in the sediments. Cesium and rubidium should exhibit close geochemical coherency also. On the basis of Z/r_h (where Z = valence, r_h = hydrated radius) potassium, rubidium, and cesium should concentrate in the sediments in relation to both sodium and lithium. Furthermore, sodium should show a greater relative concentration in the marine sediments than lithium.

GENERAL DISCUSSION

The discussion that follows will be concerned with evaluation of the analytical results and the relation of these results to our present knowledge of the abundances of the alkali metals in sediments and in igneous rocks. Emphasis will be given to the discussion of the various ratios since these probably are not affected by any systematic error present in the determinations of absolute abundances.

Meager knowledge of the sedimentological processes and products in the various areas from which the samples were obtained requires that the discussion be confined to a description of the occurrences of the elements and that only very general relationships to lithology be pointed out. Because of the several environments from which the samples came, it is believed possible to point out some general relationships between the sedimentary environment and the alkali metal content. In large part the actual relationships are functions of the provenance of the sediments as well as the environment of deposition. The provenance of some of the sediments is known in a general way; for some of the other materials the provenance cannot even be inferred.

The Rockport samples, the VLB samples, and the Mississippi Delta samples are from the Pleistocene and Recent area of the Gulf of Mexico (Lowman, 1949). The samples from both the western part and the eastern part of the Gulf of Mexico come from areas of detrital shelf sediments, from the deeper-water sediments of the continental slope and Sigsbee Deep, and from the carbonate shelf sediments. However, except for the separation of the carbonate materials from the others there has been no lithologic differentiation between the detrital shelf sediments and the deeper water sediments of the continental slope and the Sigsbee Deep.

Effect of Dried Salts on Results

Before discussion of the various ratios can properly be undertaken, it is necessary to consider the abundance of the salts left behind when the water in the cores evaporated. Table 6 summarizes the alkali metal content of sea water.

Stetson (oral communication, March, 1952) advised the author that the water content of the sediments at the top of the cores ranged from 20 to more than 200% of the dry weight of the sample. That is, if there are 100 gm of sedimentary material present in a given part of the core and its water content is 200%, there are present 200 gm of water in addition to the sedimentary material.

If the assumption is made that the average water content of the sediments is 100%, calculations show that the amounts of the alkali metals indicated in table 7 are left behind when the water evaporates from the sediment. These values show that only the sodium abundance value is affected materially by the presence of salts remaining on evaporation of the water.

Because of a wide variation in water content, depending upon the amount of clay present in the sediment, it is impossible to correct the sodium content of the sample for

TABLE 8.—*Average values corrected for sodium of sea water, assuming water content = 100%*

Samples	Average Na_2O Content	Average K_2O Content	Corrected Na_2O Content	$\frac{K_2O}{Na_2O}$ corr.
East Gulf	3.47	2.93	2.03	1.44
West Gulf	3.06	2.85	1.62	1.76
Globigerina Oozes	3.57	2.11	2.13	0.99

the sodium left as salts when the water evaporated. However, as a matter of interest, the average sodium contents of the Gulf of Mexico sediments have been corrected assuming that the water present in the materials at the time they were cored was 100 percent of the dry weight (Na_2O = 1.44%). This assumption for the average water content may be incorrect, but it is thought to be of the proper order of magnitude (table 8).

It may be seen that the potassium-sodium ratios are affected markedly by such a correction and that they approach more closely the sodium-potassium ratio of shales computed from the average chemical composition.

A relatively high sodium content in the globigerina oozes may possibly be explained by the fact that certain types of organisms concentrate sodium. Said (1951) has demonstrated that certain organisms possess the ability to concentrate sodium. He found that some calcareous foraminifera have the ability to concentrate sodium in amounts of from 0.63 to 0.95 percent Na_2O. In the same materials he found that the potassium was not appreciably concentrated and that lithium was not detectable.

Potassium-Sodium Ratio

The potassium-sodium ratios of the marine sediments center around the 0.8–0.9 class. This figure is in close agreement with the potassium-sodium ratio of 0.82 for the same two elements in igneous rocks (Rankama and Sahama, 1949). The potassium-sodium ratio of 0.7 for the sample from the Guadalupe River (GR 7 PB) is unaffected by salt contamination from the water, the quantity of sodium dissolved in river water being insufficient to affect the results.

The potassium-sodium ratios of the composite samples reveal that the sodium and potassium are present in approximately equal abundances except in two of the samples which possess a high calcium content. This is a relationship similar to that found for the two elements in the average igneous rock, although the data at hand indicate a somewhat larger ratio than that found for the average igneous rock.

Taylor (1929) and Case (cited in Kelley and Liebig, 1934) found that some oil field shales contain an unusually large amount of sodium. Taylor attempted to explain its presence by a base exchange mechanism, but Kelley and Liebig found that the sodium in clays will be replaced by the magnesium present in sea water. They came to the conclusion that a process other than base exchange must be the cause of the presence of a more than average quantity of sodium in oil field shales. Since all the composite samples contain significant quantities of organic matter, it is possible that the higher sodium content of the Austin Chalk, Eagle Ford Shale, and Miocene Nodular Shale is related to the organic matter.

Eddington and Byers (in Bradley and others, 1942) made chemical analyses of a number of samples from cores taken in the North Atlantic. They also analyzed three samples obtained from the ocean floor near Ocean City, Maryland, and eight from the Bartlett Deep in the Caribbean. The average sodium and potassium content of the materials, corrected for ignition loss, is presented in table 9.

Neither the author of the present paper nor Eddington and Byers, apparently, removed the dried salts from the sea water before making the analyses. The materials from the North Atlantic and the Bartlett Deep are enriched in sodium relative to potassium in comparison to the relations of these elements in igneous rocks. The potassium-sodium relation of the samples from off Ocean City, Maryland, is similar to that

TABLE 9.—*Atlantic ocean analyses*
(Bradley and others, 1942)

	% Na_2O	% K_2O	$\frac{K_2O}{Na_2O}$
Ocean City, Maryland	1.97	1.74	0.87
North Atlantic	1.80	1.02	0.57
Bartlett Deep	1.41	0.64	0.45

of igneous rocks. The extent to which the sediments contain the dried salts, of course, is unknown and cannot be evaluated, but even so, the comparison of the analyses with those from other areas seems warranted.

The samples from the North Atlantic have potassium-sodium ratios similar to those of the globigerina oozes from the Gulf of Mexico while the material from off the Maryland coast has a ratio similar to that of the other samples from the Gulf of Mexico. The calcium content of the samples from the North Atlantic and from the Bartlett Deep is high, being of the order of 25 to 30% CaO (45 to 55% $CaCO_3$). In contrast, the three samples from near Ocean City, Maryland, are low in calcium, having an average content of 7.7% CaO. A correlation between the calcium content and the potassium-sodium ratio is suggested from these data. This relation is to be expected since the carbonate-rich materials probably contain lesser amounts of the potassium-rich minerals than the detrital sediments.

Study of the distribution of the samples together with their sodium and potassium content indicates a correlation between lithology and the potassium-sodium ratio. In the eastern part of the Gulf, areas of sediments with a high calcium carbonate content (globigerina oozes) have a correspondingly low potassium content and a relatively high sodium content. The sodium content of the sediments from the eastern part of the Gulf of Mexico seems to remain more or less constant (3.0–4.5% Na_2O) while in the extreme eastern part the K_2O content of the sediments is low, becoming less than 1% in some places. Further correlation between lithology and the potassium-sodium ratio is seen when the samples from near Mobile, Alabama, are studied. The potassium is much lower in the sediments of this area compared with the sodium. The near-shore sediments here contain mostly detrital quartz and very little clay mineral.

Analysis of Mississippi River silt (Clarke, 1924) shows that there is an average of 1.51% Na_2O being transported as silt and 2.30% K_2O. Analyses of the water of the Mississippi River (Clarke, 1924) indicate that at Carrolton, Louisiana, the river is transporting 146 ppm as dissolved solids of which 9.3% are Na_2O and 1.9 are K_2O. The potassium-sodium ratios for the silt and for the dissolved solids are 1.5 and 0.20 respectively. These figures seem to indicate that most of the potassium is being transported as detrital and colloidal material and that the sodium is transported in solution. A large portion of the original potassium may be left behind, fixed in the soil by physio-chemical processes or by plants.

Clarke (1924) provides analyses of dissolved solids present in the waters of several rivers which drain into the eastern part of the Gulf of Mexico. The average salinity of the rivers is 67 ppm. The average sodium content of the dissolved solids is 15% Na_2O, and the average potassium content is 3.8% K_2O. The potassium-sodium ratio computed from the average values of the abundances of sodium and potassium is 0.25. This ratio indicates that most of the potassium is being transported in the detrital and colloidal matter. Similar data (Clarke, 1924) for the rivers draining into the western part of the Gulf give a potassium-sodium ratio of 0.12.

If, as is indicated by the potassium-sodium ratios for the various sediments from the Gulf of Mexico, the sodium and potassium are of about equal abundance, most of the potassium must be transported in colloidal and detrital material. The major portion of the separation of the two elements must take place in the weathering cycle rather than in base exchange within the marine environment. That this separation does occur is indicated by Goldich (1938). The sodium decreases constantly during the course of weathering whereas potassium apparently accumulates in the soil profile relative to the sodium for a short period before any significant quantity of it is removed. Examination of the hydrated radii

TABLE 10.—*Average alkali metal composition of igneous and sedimentary rocks* (Rankama and Sahama, 1949)

	Igneous Rocks	Sandstones, etc.	Shales, etc.	Limestones
% Li_2O	0.014	0.00037	0.00099	0.00056
% Na_2O	3.82	0.44	1.31	0.050
% K_2O	3.12	1.32	3.25	0.33
% Rb_2O	(0.038)[1] 0.034	0.030	0.033	—
% Cs_2O	(0.00042)[1] 0.00074	—	0.0013	—
$\frac{K_2O}{Na_2O}$	0.816	3.00	2.48	6.6
$\frac{K_2O}{Rb_2O}$	(82)[2] 92	44	98	—
$\frac{K_2O}{Cs_2O}$	(7400)[2] 4200	—	2500	—
$\frac{Rb_2O}{Cs_2O}$	(91)[2] 46	—	25	—

[1] Values given author by L. H. Ahrens, April, 1952.
[2] Ratios computed on the basis of values noted under footnote 1.

and the ionic potentials computed with the hydrated radii (table 5) suggests that such a separation should take place. The sodium with its lower electric intensity at the surface and its greater tendency toward hydration, reflected by its greater hydrated radius, should be removed before the potassium.

Potassium-Rubidium Ratio

The data presented in table 10 indicate that the potassium-rubidium ratio of an average igneous rock is 82 if the April 1952 value for the rubidium content of an average igneous rock is accepted. The average of the potassium-rubidium ratios of the sedimentary materials used in this investigation, exclusive of the composite samples, is 77. The agreement of the two values is so close that the experimental error involved in their determination is greater than the difference shown. Thus there is no positive indication of enrichment of rubidium in relation to potassium in the sediments as a whole. However, there is an implication that enrichment does occur in some of them.

If the value of rubidium content of an average igneous rock given by Rankama and Sahama (1949) is accepted, an enrichment of rubidium with relation to potassium is suggested although the difference between the values of the ratio for igneous rocks and the values of the ratio for the modern sediments is still bordering on the limits of experimental error. It would appear then, that there is no significant enrichment of rubidium with respect to potassium in the sediments as a whole.

An enrichment of rubidium relative to potassium is suggested for the Rockport-Offshore samples, but none appears to be present in the samples from San Antonio Bay. The lowest ratio is that of the Guadalupe River sample. The petrographic examination of the sample did not reveal any particular reason for the low value of the ratio. Probably the rubidium is concentrated in the clay mineral fraction of the sample, for the feldspar present is apparently of intermediate plagioclase composition.

While any conclusion based on the analysis of the one sample from the Guadalupe River can be only tentative, an interesting relation between potassium and rubidium in the weathering and sedimentological

cycles suggests itself. The low value of the potassium-rubidium ratio in this sample possibly indicates that the rubidium is enriched with respect to potassium during the weathering and transportation cycle. Probably this enrichment process, if it exists, takes the form of differential removal of potassium from the minerals during weathering, resulting in the relative concentration of the rubidium in the material remaining. When this material is moved to the marine environment, the potassium is perhaps more or less completely returned to it by adsorption from the sea water and fixation by marine organisms. Hence no apparent enrichment would be present in the marine sediments. That such a separation may possibly take place is indicated by the hydrated radii of potassium and rubidium.

The potassium-sodium ratio of dissolved solids in river waters indicates that a relatively large proportion of the potassium removed during weathering and erosion must move to the sea in colloidal and detrital material, and it is probable that even a larger proportion of the rubidium contained in any parent material does likewise.

The value of the potassium-rubidium ratio of shales computed from the average abundance of potassium and rubidium in shales is 98 (table 10). This value is essentially the same as the value obtained for the ratio in igneous rocks as given by Rankama and Sahama (1949, p. 440). These authors state that the rubidium and cesium are adsorbed into argillaceous rocks more than potassium. However, the values of the potassium-rubidium ratio for igneous rocks and for argillaceous sediments given in their table 12.8 (p. 440) contradicts this statement. Rather, the potassium-rubidium ratio for argillaceous rocks given in the table is slightly greater than that for igneous rocks.

While the statement is generally made that rubidium is enriched in argillaceous rocks, no conclusive proof seems to exist to support this statement. The basis for this statement in the literature has apparently been the analyses of shale composites made by Goldschmidt, Bauer, and Witte (1934). The data from this investigation are too scant to warrant the conclusions that are generally made from them. Neither the values given by Rankama and Sahama for the average alkali metal composition of sedimentary rocks nor the values of the potassium-rubidium ratio obtained in the present investigation indicate that any significant enrichment takes place in marine sediments. Furthermore, the values obtained from the composite samples used in the present investigation tend to support this conclusion.

Potassium-Cesium Ratio

The potassium-cesium ratio computed from the average alkali metal composition of igneous rocks is 7400 (table 10). If the value for the cesium content of an average igneous rock given by Rankama and Sahama is used in the computation of the ratio, it is 4200. The potassium-cesium ratio for shales computed from the abundance values given by Rankama and Sahama is 2500. The average value for the modern sediments is 2890, agreeing within limits of experimental error with the value from Rankama and Sahama. The average for all of the sediments outside the ten fathom line is 3210. Whether the April 1952 value of the cesium content of an average igneous rock is accepted (table 10) or whether that given by Rankama and Sahama is used for purposes of comparison, the conclusion is reached that enrichment of cesium with respect to potassium has taken place.

Comparison of the potassium-cesium ratios for the Guadalupe River sample, the samples from San Antonio Bay, and the Rockport-Offshore samples suggests a trend in the abundances of the alkali metals in the sediments. It will be noted that the potassium-cesium ratio of the Guadalupe River sample (GR 7 PB) is relatively low (1080) in comparison with the ratios for the other samples used in this investigation. The average ratio of the four San Antonio Bay samples is slightly higher (1540) than that of the Guadalupe River sample but one that is still significantly lower than the average value of the ratio for all of the samples. The Rockport-Offshore samples have an average potassium-cesium ratio which approaches the average value for all the sediments.

A separation of potassium and cesium in the weathering cycle similar to that described for the separation of potassium and rubidium is suggested, the cesium moving to the sea mainly in the colloidal and detrital material.

A third possible explanation for this apparent relationship between the fluviatile and the marine environments is that of provenance. The Guadalupe River rises in an area of sediments. If there is any concentration of cesium or rubidium in relation to the potassium in these sediments, it would be reflected in the potassium-cesium and potassium-rubidium relationships found in the sediments formed from the older sedimentary material. The cesium and rubidium would probably be further concentrated with relation to the potassium. The approach of the ratio in the Rockport-Offshore samples to that of the overall average suggests that the material in these samples is mixed with material derived from other areas. There is a strong westward-moving current along the coast in this area bringing material from the Mississippi Delta region (Goldstein, 1942).

On the basis of the values for the potassium and cesium content of average igneous rocks given in table 10, enrichment of cesium in relation to potassium by a factor of two to three is indicated. This enrichment may have taken place during several erosional and depositional cycles.

Because the cesium content of sea water is not accurately known (Goldschmidt, 1937), it is not possible to make a quantitative statement concerning the relation of the cesium being supplied to the seas, the amount that is going into the sediments, and the amount that is remaining in solution. However, it appears that the cesium brought to the seas in solution is almost entirely removed from the water, probably largely through adsorption by the minerals of the sediments. A significant portion of the cesium going to marine deposits may never be in solution, being transported in the particulate matter of the rivers.

Rubidium-Cesium Ratio

The average value of the rubidium-cesium ratio of the sediments investigated is 37, while that for the sediments from outside the ten fathom line is 40. The ratio for average igneous rocks computed from the April 1952 values given in table 10 is 91 in contrast to the value of 46 computed from the rubidium and cesium values given by Rankama and Sahama. These same authors give a rubidium-cesium abundance ratio of 25 for an average shale.

Since the relationships of rubidium and cesium to potassium in the sediments have been discussed, it will suffice to note that there is an enrichment of cesium with respect to rubidium by a factor of two to three. This relationship is to be expected when consideration is given to the relationships of the two elements to potassium. It was seen earlier that the rubidium is not significantly enriched with respect to potassium and that cesium is enriched by a factor of approximately two.

In accordance with the relations shown by rubidium and cesium in the Guadalupe River sample and in the San Antonio Bay samples, the rubidium-cesium ratio of these sediments suggest that their cesium content is higher in proportion to the rubidium than that found in the marine sediments. The scant data suggest that the rubidium is adsorbed onto the minerals in the marine environment in greater quantity than the cesium; this relationship exists because a proportionately greater quantity of the cesium is probably carried to the marine deposits in the detrital and colloidal materials. It appears then that the potassium is removed during the weathering process in relatively greater quantities than the rubidium, and that the rubidium is removed from the parent materials in proportionately greater amounts than the cesium. In the marine environment the cesium in solution is preferentially adsorbed in relation to the potassium and rubidium, and thus cesium is enriched in relation to them.

Comparison of the potassium-rubidium and the potassium-cesium ratios of the various samples indicates that there is no regularity of occurrence of the three elements. The data seem to suggest that while there is a general enrichment of cesium with respect to potassium and rubidium in sedimentary materials, the relation depends to a large extent upon the sediments themselves and that it is not always constant. Much must depend upon the previous history of the sedimentary material.

The statement that the enrichment of cesium with respect to potassium and rubidium may be attributed to the relations shown by the hydrated radii alone must be questioned when one considers the fact that the percentage difference, based on the

smaller ion, between the hydrated radii of potassium and rubidium is approximately equal to the percentage of difference between the hydrated radii of rubidium and cesium (table 5). It would seem that there should be a progressive enrichment in each of the elements in going from potassium to rubidium to cesium and that the enrichment of rubidium with respect to potassium should be of the same order of magnitude as the enrichment of cesium with respect to rubidium. However, in the sediments studied and the ones for which analyses are reported in the literature, there does not appear to be any significant enrichment of rubidium with respect to potassium while there is a very marked enrichment of the cesium with respect to the potassium and rubidium.

There may be several reasons for this apparent anomalous behavior of these members of the alkali metal group. One may be that the values of the hydrated radii are incorrect. Possibly the values for the cesium and rubidium content of an average igneous rock are wrong. There may have been a different bias introduced into the analyses for the cesium, rubidium, and potassium contents of the igneous rock. The bias may not be the same for the determinations for igneous rocks and for the determinations for sediments.

Factors other than the hydrated radii and the ionic potential computed on the basis of the hydrated radii may be important in the separation of the elements. The fact that the cesium ion is relatively unhydrated whereas the potassium and rubidium ions are hydrated may be important. The ionic potential of the unhydrated ion may control its release from the minerals. That the ionic potential is important in controlling the release of the ions seems to be suggested by the relations of the lithium to sodium. Part of the concentration may come about during the weathering cycle with the separation of the more easily hydrated potassium from the rubidium and the rubidium from the cesium. That potassium and rubidium both enter the illite structure in preference to cesium is suggested by the results of the differential thermal analyses described earlier. A preferential adsorption of rubidium in illite is suggested from these same analyses. This adsorption may occur in the weathering cycle. The potassium-cesium ratios of the samples containing large fractions of illite were higher than those of the samples containing more detrital material and other clay minerals. This relation suggests that the cesium may be in effect concentrated in the detrital minerals.

In considering the problem of the relative enrichment of the cesium, one must give some thought to the fact that a large part of the sedimentary material was not derived from igneous rocks but from sedimentary rocks. The enrichment may be the result of more than two cycles of weathering and sedimentation, although a similar enrichment in rubidium might also be expected.

Inasmuch as the knowledge of the behavior of rubidium and cesium in weathering is very limited, if not non-existent, it does not seem appropriate to draw any definite conclusions as to the reason for the enrichment. For the occurrence of the less abundant alkali metals in marine sediments to be understood, their behavior in the weathering cycle needs to be studied.

Lithium Content

Since lithium is not closely associated with the rest of the alkali metals geochemically, it must be discussed in terms of absolute abundance rather than in terms of ratios. The average lithium content of all the Recent sediments investigated is 0.013% Li_2O. This value corresponds closely with the value given by Rankama and Sahama (1949) for the lithium content of igneous rocks. Within the bounds of experimental error there seems to be no essential difference between the value quoted by Rankama and Sahama for the average lithium content of shales and the average value obtained in this investigation. Even the globigerina oozes contain lithium in amounts which correspond closely with those found in the average igneous rock.

The lithium apparently does not follow the other alkali metals in the weathering cycle, but replaces Mg^{++} and Fe^{++} in the clay mineral structures. Mitchell (cited in Rankama and Sahama, 1949) found a very definite enrichment of lithium in some soils. This fact suggests that the lithium is concentrated relative to the other alkalies in the weathering process and that it is transported to the marine environment in the

TABLE 11.[1]—*Results of the spectrochemical analyses*

Sample No.	Weight Loss on Ignition %	Weight Percent Corrected to 110° C.				
		Na_2O	K_2O	Rb_2O	Li_2O	Cs_2O
		Gulf of Mexico Samples				
EG 1-B	3.54	4.39	2.88	0.039	0.013	0.00066
EG 1-C	5.05	3.66	2.91	0.039	0.014	0.00094
EG 2-B	4.80	3.58	2.88	0.042	0.012	0.0010
EG 2-C	3.61	2.72	2.86	0.039	0.013	0.00085
EG 3-B	2.71	2.46	2.69	0.042	0.0097	0.0013
EG 3-C	3.14	3.49	2.64	0.038	0.017	0.00097
EG 4-B	3.66	3.72	2.81	0.038	0.011	0.0011
EG 4-C	4.44	4.14	2.54	0.033	0.016	0.00082
EG 6-B	3.62	4.64	4.34	0.049	0.014	0.00054
EG 6-C	1.87	3.56	3.07	0.041	0.018	0.00096
EG 9-A	4.44	3.47	2.92	0.039	0.014	0.00086
EG 9-B	1.73	3.37	2.52	0.032	0.013	0.00056
EG 9-C	2.14	2.50	3.02	0.039	0.015	0.00095
EG 12-A	5.82	2.26	2.02	0.033	0.017	0.00057
EG 12-B	4.07	4.18	2.68	0.037	0.018	0.00077
EG 12-C	4.70	4.03	2.52	0.033	0.014	0.0011
EG 15-A	4.36	3.34	2.50	0.035	0.010	0.00082
EG 15-B	4.40	2.77	2.29	0.030	0.0089	0.0010
EG 15-C	4.63	3.05	2.88	0.033	0.018	0.00047
EG 99-A	5.72	3.30	3.43	0.040	0.015	0.0014
EG 99-B	5.79	3.26	3.42	0.038	0.014	0.0010
EG 99-C	5.04	2.92	2.74	0.030	0.025	0.0010
EG 103-A	6.86	2.94	3.82	0.038	0.015	0.0011
EG 103-B	5.15	3.16	2.54	0.027	0.019	0.00095
EG 103-C	5.04	5.04	2.81	0.032	0.016	0.00071
EG 105-A	5.26	3.72	3.65	0.038	0.013	0.00095
EG 105-B	5.88	4.14	3.80	0.040	0.015	0.0012
EG 105-C	6.03	3.03	3.71	0.045	0.015	0.00094
EG 106-A	5.64	3.79	3.58	0.038	0.011	0.0011
EG 106-B	3.87	4.93	3.44	0.038	0.019	0.00074
EG 106-C	5.13	3.56	3.16	0.038	0.015	0.00089
EG 107-B	3.57	2.84	2.83	0.034	0.010	0.00065
EG 107-C	3.81	3.04	3.34	0.035	0.014	0.00074
EG 108-B	6.25	4.34	3.41	0.038	0.022	0.00065
EG 108-C	7.04	3.48	3.00	0.035	0.018	0.00063
EG 109-B	5.19	3.91	3.51	0.041	0.020	0.00076
EG 109-C	3.14	3.06	3.19	0.034	0.018	0.00047
EG 111-A	4.85	3.59	2.95	0.031	0.013	0.00040
EG 111-B	6.36	3.83	3.80	0.036	0.015	0.00060
EG 111-C	5.61	2.98	3.00	0.035	0.014	0.00042
EG 212-A	5.98	4.23	3.05	0.035	0.024	0.00055
EG 215-A	5.16	3.68	3.08	0.038	0.018	0.00063
EG 218-A	3.80	3.46	2.33	0.033	0.016	0.00039
EG 221-A	3.22	1.79	0.49	0.0097	0.0071	Trace
EG 225-A	6.86	2.56	0.80	0.016	0.024	Trace
WG 140-A	5.86	2.99	3.01	0.040	0.015	0.0014
WG 140-B	4.77	3.15	3.73	0.050	0.012	0.0019
WG 140-C	4.80	3.04	3.32	0.038	0.013	0.0013
WG 145-B	1.00	2.67	3.10	0.031	0.011	0.0013
WG 147-A	3.44	2.21	3.05	0.039	0.0081	0.0013
WG 147-B	4.74	1.62	3.34	0.051	0.011	0.0014
WG 149-A	2.73	2.42	3.81	0.043	0.013	0.00092

[1] EG = East Gulf
WG = West Gulf
A is surface sample, B is 75 cm depth, C is 150 cm depth.

[2] Not detectable.

[3] S 57-A, S 91-A and S 133-A are from San Antonio Bay. GR 7 PB is from Guadalupe River, Highway 35 crossing, Aransas County, Texas. J 32-A, J 35-A, and J 36-A are Rockport-Offshore samples.

TABLE 11—*continued*

Sample No.	Weight Loss on Ignition %	Weight Percent Corrected to 110° C.				
		Na_2O	K_2O	Rb_2O	Li_2O	Cs_2O
		Gulf of Mexico Samples—continued				
WG 149-B	2.78	2.14	3.24	0.034	0.0084	0.00050
WG 153-A	3.42	4.00	3.24	0.036	0.016	0.0013
WG 153-B	4.17	3.27	2.98	0.038	0.012	0.0011
WG 422-A	2.45	1.91	1.38	0.020	0.0072	N. D.[2]
WG 480-A	3.56	3.38	3.32	0.037	0.012	0.0022
WG 485-A	5.78	3.44	3.54	0.035	0.014	0.0016
WG 515-A	12.7	1.78	1.67	0.022	0.015	0.00061
WG 515-B	3.26	2.74	2.30	0.035	0.016	0.00052
WG 515-C	4.47	2.46	2.96	0.053	0.018	0.00089
WG 532-A	3.02	3.25	3.25	0.063	0.016	0.0013
WG 532-B	3.48	3.18	2.88	0.038	0.015	0.00077
WG 532-C	1.67	3.96	2.68	0.037	0.015	0.00083
WG 538-A	4.71	3.38	2.91	0.038	0.0080	0.0010
WG 538-B	3.76	4.66	3.32	0.057	0.015	0.0014
WG 542-A	6.56	3.55	1.88	0.032	0.0097	0.00052
WG 542-B	5.20	3.64	3.33	0.040	0.015	0.0013
WG 542-C	7.29	3.32	3.05	0.051	0.010	0.0011
WG 545-B	5.14	3.56	2.59	0.036	0.023	0.0011
WG 545-C	4.93	3.07	2.28	0.041	0.013	0.00063
WG 549-A	4.94	3.52	2.93	0.048	0.0089	0.0012
WG 549-B	4.54	3.08	1.48	0.018	0.011	Trace
WG 549-C	4.92	3.04	2.65	0.035	0.011	0.00071
WG 550-B	2.12	4.51	2.74	0.030	0.014	0.00063
WG 550-C	3.92	2.84	2.55	0.028	0.012	0.00048
WG 551-B	5.51	3.22	2.68	0.036	0.016	0.00080
WG 551-C	4.09	3.14	2.88	0.041	0.014	0.00044
		Globigerina Oozes				
WG 545-A	3.39	3.09	4.45	0.045	0.010	0.0017
WG 550-A	3.05	2.91	1.81	0.020	0.0097	0.00053
WG 551-A	3.99	3.36	3.94	0.042	0.0096	0.0012
EG 1-A	3.23	3.10	2.37	0.025	0.0046	0.00067
EG 2-A	3.45	3.24	2.00	0.027	0.0095	0.00079
EG 3-A	3.78	4.90	3.74	0.040	0.016	0.0012
EG 4-A	4.18	5.28	2.97	0.038	0.026	0.0011
EG 6-A	4.03	4.15	2.74	0.027	0.011	0.00085
EG 107-A	3.64	3.86	2.60	0.028	0.0092	0.00075
EG 109-A	1.88	2.16	0.62	0.0080	0.0057	N. D.
EG 128-A	3.50	3.57	0.82	0.011	0.011	Trace
EG 137-A	3.75	4.42	3.26	0.038	0.020	0.0012
EG 146-A	6.16	3.66	2.54	0.032	0.017	0.00094
EG 149-A	4.84	4.27	1.18	0.017	0.021	Trace
EG 151-A	3.93	2.69	0.63	0.0087	0.0069	N. D.
EG 153-A	7.55	2.22	0.20	0.030	0.0077	N. D.
EG 185-A	5.49	3.87	1.53	0.021	0.016	0.0003
EG 187-A	6.34	4.04	2.06	0.021	0.019	N. D.
EG 190-A	5.45	3.12	0.95	0.014	0.016	Trace
		Mississippi Delta Samples				
MP 112-51 ABL 130 cm.	3.26	1.80	1.48	0.020	0.0097	0.00079
MP 115-51 ABL 130 cm.	3.85	2.23	1.43	0.020	0.013	0.00071
MP 122-51 ABL 0 cm.	2.93	1.78	0.90	0.013	0.0071	0.00047
MP 123-51 ABL 0 cm.	4.14	1.50	0.65	0.0087	0.0059	Trace
MP 123-51 ABL 40 cm.	4.85	1.66	0.78	0.012	0.0079	N. D.

TABLE 11—*continued*

Sample No.	Weight Loss on Ignition %	Weight Percent Corrected to 110° C.				
		Na_2O	K_2O	Rb_2O	Li_2O	Cs_2O
		Mississippi Delta Samples—continued				
MP 123-51 ABL 130 cm.	1.96	1.20	0.27	0.0040	0.0038	N. D.
MP 128-51 ABL 0 cm.	3.84	1.44	0.47	0.0069	0.0066	Trace
MP 128-51 ABL 130 cm.	4.59	1.69	0.70	0.0092	0.0069	Trace
MP 135-51 ABL 0 cm.	4.96	1.90	1.11	0.017	0.011	0.00063
MP 135-51 ABL 130 cm.	1.28	0.96	0.19	0.0027	0.0030	Trace
MP 137-51 ABL 0 cm.	4.40	1.40	0.65	0.0095	0.0061	N. D.
MP 137-51 ABL 130 cm.	3.32	1.63	0.72	0.0097	0.0083	Trace
BS 107-51 ABL 65–71 cm.	4.70	2.46	1.97	0.023	0.013	0.00088
BS 107-51 ABL 100–105 cm.	4.52	1.69	1.38	0.018	0.011	0.00073
		VLB Samples				
VLB 31c-9	2.25	2.40	1.92	0.031	0.015	0.00048
VLB 31c-10	3.44	2.25	1.74	0.025	0.011	0.00048
VLB 31c-11	1.73	2.16	1.64	0.024	0.010	0.00044
VLB 43c-1a	1.66	0.99	1.79	0.021	0.026	0.00060
VLB 43c-2a	1.27	2.08	2.25	0.024	0.012	0.00035
VLB 43c-2b	2.52	1.95	2.37	0.031	0.013	0.00056
VLB 43c-2c	3.91	1.40	1.53	0.023	0.012	0.00085
VLB 43c-3b	1.90	2.26	1.86	0.028	0.0083	0.00044
VLB 43c-4a	6.19	2.40	1.48	0.026	0.010	0.00039
VLB 43c-4c	2.23	2.35	1.79	0.027	0.011	0.00058
VLB 43c-5a	3.34	1.93	1.89	0.029	0.017	0.00073
VLB 43c-5b	2.01	3.01	1.51	0.028	0.012	0.00033
		Rockport, Texas: San Antonio Bay and Offshore Samples[3]				
S 57-A 0–5 cm.	1.88	1.94	2.19	0.028	0.0047	0.0011
S 91-A 10–15 cm.	2.27	0.85	1.21	0.016	0.0038	0.00087
S 91-A 20–25 cm.	3.94	1.23	2.26	0.026	0.045	0.0013
S 133-A 12–16 cm.	7.94	0.96	1.95	0.032	0.013	0.0018
GR 7 PB	3.57	0.55	0.42	0.0080	0.0044	0.00039
J 32-A	3.88	2.23	1.25	0.019	0.0076	N. D.
J 35-A	3.81	3.30	1.67	0.038	0.010	0.00077
J 36-A	2.70	2.16	2.00	0.020	0.0092	0.00087
		Composite Samples				
Austin Chalk	2.16	6.36	2.45	0.022	0.0065	Trace
Cherokee	5.54	1.20	1.59	0.020	0.0095	0.00062
Eagle Ford Shale	3.82	0.58	0.25	0.0028	0.0035	N. D.
Lower Eutaw	3.72	1.38	1.69	0.023	0.014	0.00087
Miocene Nodular	9.45	1.69	1.13	0.011	0.0053	Trace
Selma Chalk	4.32	1.50	1.75	0.020	0.014	0.00089
Tuscaloosa sandstone	3.47	1.04	1.12	0.017	0.011	0.00061

colloids and the detrital material. From consideration of the hydrated radius and the electric intensity at the surface of the hydrated ion, lithium should be removed preferentially from the minerals in relation to the other alkali metals. However, lithium behaves differently, making this relationship merely an apparent one. The behavior of lithium in the weathering and sedimentary cycle is probably controlled to a large extent by its ionic radius. Having a smaller ionic radius than the other alkali metals, it may be held more tightly in the mineral structure than any of them. Its structural position in the ferro-magnesian minerals may cause it to be relatively less easily hydrated than the other alkali metals and to remain behind when the other elements of the group are removed during weathering. Goldich (1938) has shown that magnesium and iron are removed less rapidly than are sodium and potassium in the weathering of a granite gneiss. In general lithium follows magnesium in the weathering cycle and is found in the clay minerals and other minerals providing octahedral coordination sites.

A correlation between the montmorillonite content of the sediments and the lithium content is suggested by the results of the thermal analyses. Most of those samples which contain predominantly montmorillonite exhibit a greater content of lithium than those samples with no montmorillonite. Since Mg^{++} may occur in illite, Li^{+} may occur in illite also.

The results of this investigation fail to support the statement of Rankama and Sahama (1949, p. 428) that the deep sea sediments possess a greater lithium content than the near-shore sediments. The comparison of the lithium content of the sediments along the Ship Shoal and Mobile II traverses (fig. 1) indicates no such relationship between the lithium content of the sediments and their distance from shore or with water depth. The lithium content of the sediments seems more closely related to the provenance of the sedimentary material.

General Occurrence in Sediments

As far as is known at the present time the alkali metals are closely associated with the clay fraction of the sediments. They may be concentrated in the clay minerals by adsorption through the medium of base exchange and by entrance into structural positions. The role of the alkali metals during the actual formation of clay minerals, whether it be in an environment of subaerial weathering or in the marine environment, is inadequately known. The alkali metals are also apparently concentrated by marine organisms and plants and by authigenic processes. Adsorption of potassium by montmorillonite to form illite has been suggested as a means for the removal of potassium from sea water. However, Grim, Dietz, and Bradley (1949) have found montmorillonite and illite in approximately equal abundance in some Recent sediments, with no evidence being present of a change either in depth below the sea floor or in distance from shore. They suggest that the conversion to illite may be a metamorphic rather than a diagenetic process.

The actual relative concentration of the elements is probably dependent upon the extent of the decomposition of the minerals in the parent rock during weathering, a greater concentration of cesium relative to potassium and rubidium occurring when there is extensive chemical weathering.

Stetson (oral communication March, 1952 suggested to the author that the alkali metal content of the cores from the eastern part of the Gulf of Mexico may possibly be related to the lowering of the sea level during Pleistocene time. He stated that little if any carbonate material is being derived from the Florida peninsula at the present time and that all of the sediment in the area apparently represents material reworked when the seas advanced after the Pleistocene glaciations. Weathering during a period of lowered sea level could have produced a concentration of clay materials which would be reflected in the present sediments.

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REFERENCES

AHRENS, L. H., 1950, Spectrochemical analysis. Addison-Wesley Press, Cambridge, Massachusetts, 269 p.

BOYD, G. E., SCHUBERT, J., AND ADAMSON, A. W., 1947, Ion-exchange equilibria on ion exchange resins: Jour. Am. Chemical Soc., v. 69, p. 2818–2829.

BRADLEY, W. H. AND OTHERS, 1942, Geology and biology of North Atlantic deep-sea cores: U. S. Geol. Survey Prof. Paper 196.

CANNEY, F. C., 1952, Some aspects of the geochemistry of potassium, rubidium, cesium, and thallium in sediments: Ph.D. Thesis, Massachusetts Institute of Technology, Department of Geology.

CLARKE, F. W., 1924, The data of geochemistry: U. S. Geol. Survey Bull. 770.

FAIRBAIRN, H. W. AND OTHERS, 1951, A cooperative investigation of precision and accuracy in chemical, spectrochemical, and modal analysis of silicate rocks: U. S. Geol. Survey Bull. 980.

GOLDICH, S. S., 1938, A study of rock weathering: Jour. Geology, v. 46, p. 17–58.

GOLDSCHMIDT, V. M., BAUER, H. AND WITTE, H., 1934, Zur geochemie der alkali-metalle II: Nachr. Ges. Wiss. Gottingen, IV, N.F. 1, no. 14.

GOLDSCHMIDT, V. M., 1937, The principles of distribution of chemical elements in minerals and rocks: Jour. Chemical Soc. (London), p. 655–675.

GOLDSTEIN, A., JR., 1942, Sedimentary petrologic provinces of the northern Gulf of Mexico: Jour. Sedimentary Petrology, v. 12, p. 77–84.

GREENMAN, N. N. AND LE BLANC, R. J., 1956, Recent marine sediments and environments of northwest Gulf of Mexico: Am. Assoc. Petroleum Geologists Bull., v. 40, p. 813–847.

GRIM, R. E., DIETZ, R. S., AND BRADLEY, W. F., 1949, Clay mineral composition of some sediments from the Pacific Ocean off the California coast and the Gulf of California: Geol. Soc. America Bull., v. 60, p. 1785–1808.

HANDBOOK OF CHEMISTRY AND PHYSICS, 1945, 29th ed., Chemical Rubber Publishing Co., Cleveland, 2640 p.

KELLEY, W. P., AND LIEBIG, G. F., JR., 1934, Base exchange in relation to composition of clay with special reference to effect of sea water: Am. Assoc. Petroleum Geologists Bull., v. 18, p. 358–367.

LOWMAN, S. W., 1949, Recent sedimentation in the Gulf Coast area: Am. Assoc. Petroleum Geologists Bull., v. 33, p. 1939–1997.

NACHTRIEB, N. H., 1950, Spectrochemical analysis. McGraw-Hill, New York, 128 p.

RANKAMA, K. AND SAHAMA, TH. G., 1949, Geochemistry. University of Chicago Press, Chicago, 911 p.

SAID, RUSHDI, 1951, Preliminary note on the spectroscopic distribution of elements in the shells of some recent calcareous foraminifera: Contributions from Cushman Foundation for Foraminiferal Research, v. 2, part I, p. 11–12.

STETSON, H. C., 1949, Sediments of the western half of the Gulf of Mexico (abs.): Oil and Gas Journal, v. 47, no. 46, p. 150.

———, 1953, The sediments of the western Gulf of Mexico, Part I, The continental terrace of the western Gulf of Mexico: Papers in physical oceanography and meteorology published by Massachusetts Institute of Technology and Woods Hole Oceanographic Institution, v. 12, no. 4.

SVEDRUP, H. U., JOHNSON, M. W., AND FLEMING, R. H., 1942, The oceans. Prentice-Hall, New York, 1087 p.

TAYLOR, E. M., 1929, The replaceable bases in shales and clays overlying petroliferous strata: Jour. Institute Petroleum Technology, v. 15, p. 207–210.

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FIGS. 1–12, DECEMBER, 1958

DISPLACEMENT OF MICROFOSSILS[1]

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ABSTRACT

The phenomena of horizontal and vertical displacement of microfossils are re-examined in the light of their increasing importance in correlation work and in paleoecologic studies. Size ranges of the common micropaleontological objects are tabulated and classified in terms of Wentworth's grade scale of sedimentary particles. The following types of displacement are discussed, and examples of each are cited:

I. Natural displacement
  A. Vertical displacement
    1. Older fossils into younger beds (redeposition)
    2. Younger fossils into older beds (stratigraphic leak)
  B. Horizontal displacement (environmental mixing)
    1. Intracontinental displacement
    2. Intramarine displacement
    3. Displacement between marine and continental environments
II. Artificial displacement (contamination)
  A. Displacement during sampling operations
  B. Displacement in the laboratory

The principal agents of natural displacement are waves and currents, running water, ground water, wind, glacial ice, and organisms of various types. Vertical displacement is most significant in the use of microfossils for stratigraphic work, whereas horizontal displacement must be taken into account in paleoecological investigations. Possible criteria for recognition of displaced microfossils are listed and discussed.

INTRODUCTION

The present paper attempts to evaluate and analyze the significance of displacement of microfossils in terms of their increasing importance both in stratigraphic correlation and in paleoecological investigations. Because of their small size they are easily transported by a variety of geologic and biologic agents and may be displaced either vertically or horizontally from their environments of life or from their place of entombment.

Reworking of microfossils has been known for a long time, and although the phenomenon is quite common, it need not impair or deter the widespread use of micropaleontological objects in geological interpretations, provided the nature of the phenomenon is recognized and understood. In succeeding sections of this paper the principal types of horizontal and vertical displacement will be described, the mechanisms by which the displacement is accomplished, and suggested criteria for recognition of displaced fossils or faunas will be given.

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Biocoenose and Thanatocoenose

Shrock and Twenhofel (1953, p. 22) defined the biocoenose as the assemblage of organisms which live and flourish in a given environment under a given combination of physical and biochemical factors.

The remains of such a faunal association or biofacies would, if preserved in place, offer valuable clues to the environment of deposition of the enclosing sediments. The assemblage of fossil remains which is commonly encountered in a given sedimentary unit, however, is one assembled in a particular site of deposition after death and before entombment—the thanatocoenose (Shrock and Twenhofel, 1953, p. 22). Thus the thanatocoenose may represent (1) an accumulation of remains of organisms formed in the normal environment of the biocoenose, (2) an accumulation of organic remains resulting from the killing off of large populations by some catastrophic change in one or more of the environmental factors, or (3) an assemblage of sedimentary particles of various sizes, including the remains of microorganisms and skeletal parts of larger organisms, transported into the site of

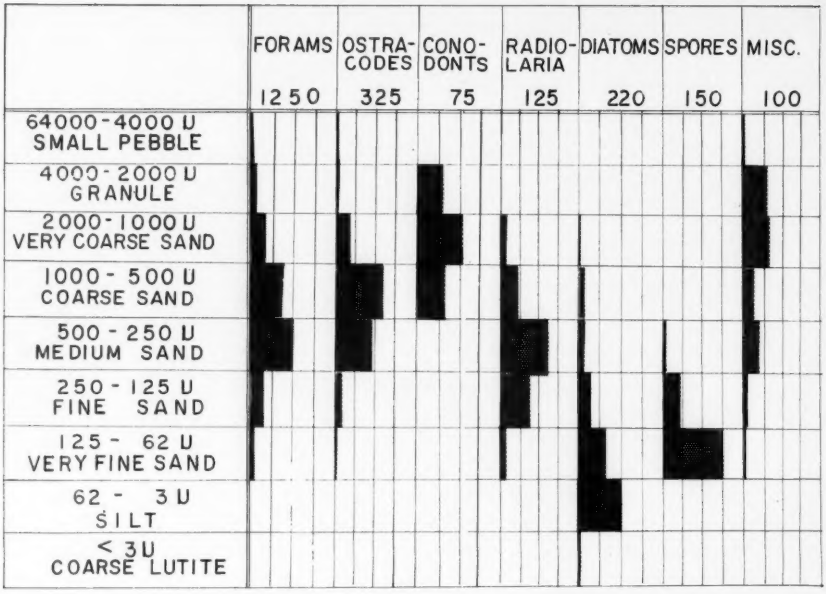


FIG. 1.—Grain size distribution of some common groups of microfossils, based on measurements of 1500 specimens.

entombment, and forming a part of the sedimentary deposit. The thanatocoenose may commonly consist of elements of all three of the above assemblages and can be interpreted only as those remains of organisms which were enclosed in the sediment at the time of deposition and diagenesis.

Microfossils as Sedimentary Particles

The tests of microorganisms and dissociated skeletal elements of larger organisms must be considered as sedimentary particles when the organisms died and can no longer control their movements. Figure 1 shows the distribution of some of the common microfossils in terms of Wentworth's grade scale of particle sizes. The tabulation is based on a sampling of the measurements of over 1500 species of various microfossils taken from published papers, and although the number sampled is small, it does give a fair approximation of the size ranges of some typical microfossils.

It will be observed from figure 1 that most of the tests of Foraminifera are particles within the range of very coarse to medium sand (1000 microns to 250 microns). The ostracodes generally fall into this grade size range. There is considerable variation in the size of such miscellaneous microfossils as bryozoan fragments, remains of echinoderms, and immature mollusks, most of them ranging from small pebbles, through granules, to coarse and medium sand.

Approximately 90 percent of the conodonts fall within the range of 2000 microns (granules) to 500 microns (coarse sand).

Radiolarian tests are essentially of the size range from 250 microns to 62 micron (very fine sand and silt), diatom frustules are primarily silt-sized particles ranging from 125 microns (very fine sand) to 3 microns in minimum dimension (lower limit of silt). Most of the spores and pollens, dinoflagellates, silicoflagellates, hystrichospherids, and microforaminifera also fall into the latter category (very fine sand to various grades of silt and coarse lutite).

In addition to the size of the microfossil, other parameters which may influence the ease with which it may be transported are (1) specific gravity, (2) chambering with

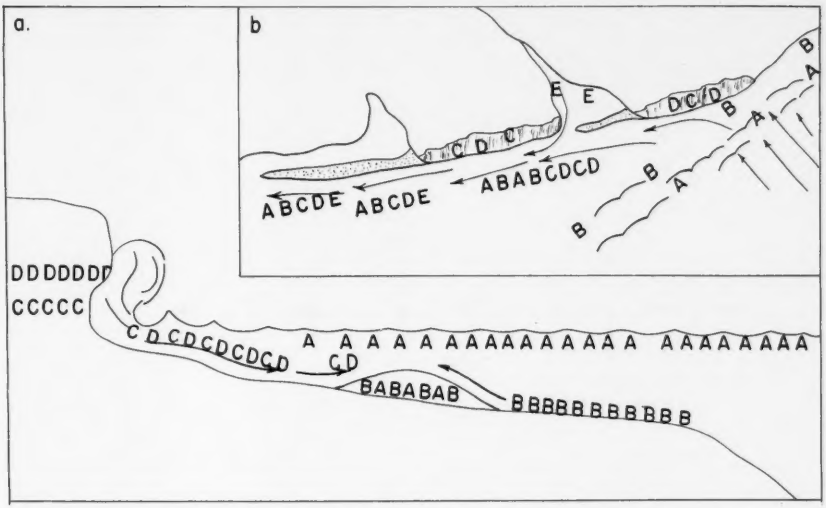


FIG. 2.—Displacement of microfossils along a shoreline: a. redeposition by wave erosion of fossiliferous strata exposed along the shoreline of an ocean or large lake, b. lateral displacement by action of littoral currents.

air spaces, (3) shape of the particle, (4) difference in specific gravity of the particle and that of the transporting medium, and (5) the viscosity of the medium. It is strongly suspected that the shape and buoyancy effects of chambering are more significant in the case of larger microfossils in aqueous media, and are only significant among the smaller microfossils in the case of eolian transport.

MECHANICS OF NATURAL DISPLACEMENT

Displacement of micropaleontological objects is usually accomplished by one or more of several natural agencies. These are, in approximate order of importance: (1) nearshore waves and currents in the sea and in large lakes, (2) turbidity currents, (3) streams, (4) ground water, (5) wind, (6) organisms, (7) glaciers and (8) miscellaneous processes. These agencies of erosion, transportation, and deposition accomplish the following types of displacement:

1. Vertical displacement
   - A. Older microfossils into younger zones (redeposition)
   - B. Younger microfossils into older zones (stratigraphic leak)
2. Horizontal displacement (environmental mixing)
   - A. Intracontinental displacement
   - B. Intramarine diaplacement
   - C. Displacement between marine and continental environments.

Vertical displacement, either from older to younger, or from younger to older zones, may also involve environmental mixing.

The rocks from which the microfossils are derived may be exposed to weathering, thus releasing the microfossils into the weathered mantle rock, or the rocks may be eroded by corrosion or corrasion to liberate them for transportation.

The essential mechanics of microfaunal displacement by each of the above mentioned agencies is briefly reviewed below.

Nearshore Wave and Current Action

Waves, undertow, rip currents, and littoral currents accomplish faunal displacement in a number of ways (fig. 2). Horizontal displacement of faunas in the sea, and in large lakes, reworking of older fossils into younger beds, and displacement of younger fossils into older beds are common. Ellison (1951) has discussed the nature of some of these displacements, particularly

the displacement of shallow-water faunas into deeper water.

The quarrying and abrasive action of waves against sea cliffs and other bedrock exposures of older fossiliferous strata is responsible for many cases of redeposition of microfossils. (fig. 2a). For example, the foraminifer-rich bluff of Miocene sediments along the western edge of Pamlico Sound is being attacked at present by waves and streams, furnishing abundant Miocene Foraminifera and ostracodes into the modern faunal assemblage of the sound and adjacent continental shelf (Coryell, 1956, personal communication). Hedberg (1956, personal communication) has described to the writer the occurrence of cliffs of Oligocene and Miocene shales along the coast of eastern Falcon Province, Venezuela, which the waves are attacking and reworking the Oligocene and Miocene Foraminifera into the recent beach sands. Carrigy (1956) describes the derosion of Pleistocene dune ridges of Foraminifera into the sill area of Warnbro Sound on the coast of Western Australia. In this instance a line of Pleistocene dunes forming a sill separating the waters of the sound from the Indian Ocean is being reworked by wave action into the modern sediments both seaward and landward.

In areas of emerging coastlines, the sediments previously deposited nearshore become a part of the material attacked by the waves of the nearshore environment in which the next highest formation is being deposited, hence reworking of the microfossils is quite common. For example, the extremely rich and varied fauna of the Pleistocene Lomita Formation of southern California contains many specimens of foraminifers derived from the previously deposited Pliocene beds in the same region (Bandy, 1952; Crouch, 1954).

Longshore or littoral currents are also responsible for redeposition as well as horizontal displacement of microfossils. Figure 2b demonstrates the lateral displacement and redeposition of microfaunas accomplished by this mechanism.

Wave action along the shore of a transgressing sea over an area of comparatively low relief is responsible for a very common form of displacement. Many examples of this form of displacement are found in the Cretaceous and Tertiary of the Gulf Coast. The waves and currents of the transgressing sea (fig. 3) pick up and incorporate into its sediments both the forms weathered from older rocks and material actually derived from wave and current action on the unweathered rocks. The basal Red Bluff glauconitic sand of Oligocene age near Hiwanee, Mississippi, contains numerous Foraminifera reworked from the Cretaceous Austin, Taylor, and Navarro Groups (Coryell, 1956, personal communication). Also, fragments of the Vicksburg Limestone and Vicksburg Foraminifera occur in the overlying Bucatunna Clay in southeastern Mississippi and southwestern Alabama. (Denham, 1956, personal communication.)

In some instances, stratigraphic leaks may occur when a transgressing sea encroaches over a limestone terrane rendered porous and permeable by ground water solution and by weathering. The microfossils of the near-shore zone of the advancing sea are dropped into the porous areas, and if the sediments filling in the irregularities of the limestone surface are also calcareous, serious misinterpretations of the age of the limestone may result. The writer knows of one such instance in which a core from an otherwise unfossiliferous dolomitic limestone was examined and found to contain one excellent specimen of a fusulinid. On the basis of this determination, the enclosing rock was identified as Pennsylvanian in age. Actually the fusulinid was in a small calcite-filled crevice in a Cambro-Ordovician dolomite.

The deposition of shallow-water benthonic remains and planktonic microfossils on beaches is quite common. In his collections the writer has samples of the calcarenite beach sands from St. Thomas, V.I., which are composed of microcoquina, echinoid spines, and several species of peneroplid Foraminifera. Also, in many areas along the Pacific Coast of the United States, the spring floods of diatoms frequently accumulate on the beach in sufficient quantities to form a deposit several inches thick and of great extent. The beach sands at many localities along the Atlantic and Gulf Coasts contain many shallow-water benthonic Foraminifera as well as planktonic forms. The beach sands at Galveston, Texas, and at Nantasket Beach, Mass., are well-known

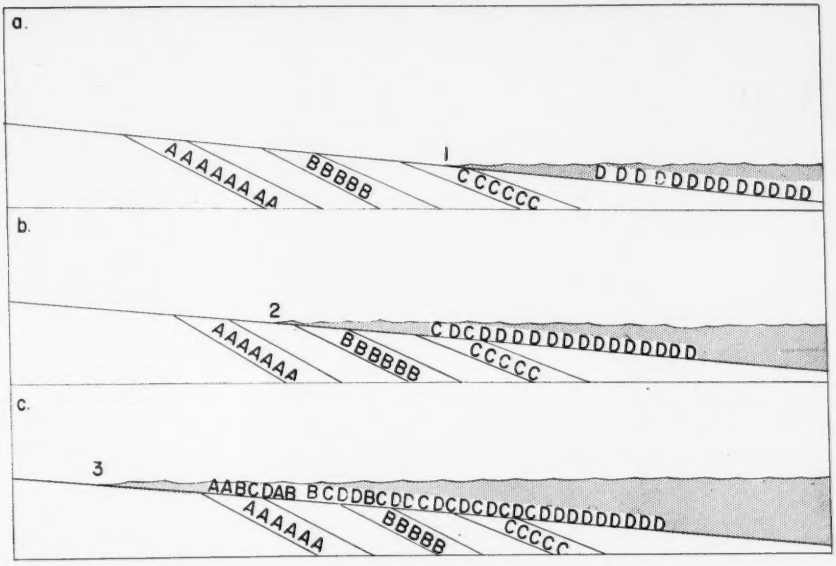
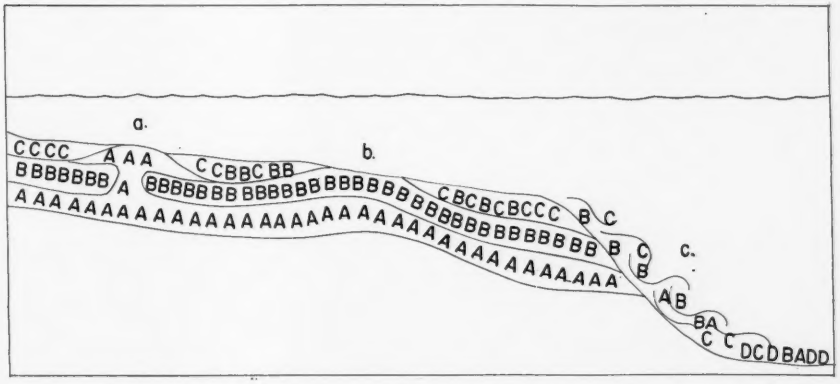


FIG. 3.—Redeposition by incorporating fossils into sediments of a sea advancing over exposures of older fossiliferous strata (3 progressive stages shown).

examples of environmental displacement of fossils by wave action.

Submarine wave erosion of older strata exposed along the flanks of seamounts, guyots, and other subaqueous outcrops is a common form of redeposition of microfossils (fig. 4). Revelle and Shepard (1955) describe Foraminifera from the Pliocene Repetto Formation occurring in the deep saddle between San Clemente Island and Cortez Bank off the coast of Southern California. The source of the reworked microfossils is a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series of submarine exposures of the Repetto on the flanks of the trough which is being eroded and the fossils reworked by waves and currents. Off the Atlantic Coast of North Carolina, shell fragments and Foraminifera derived from the Pliocene and Pleistocene coquina beds are being eroded subaqueously and redeposited nearshore by waves during violent storms. Natland (1933) describes Miocene Foraminifera occurring in the nearshore sediments of southern California west of Long Beach derived from Miocene beds under attack by submarine wave erosion.

Littoral and rip currents also play a role in redistributing laterally the microfossils which have been transported into the nearshore marine environment by streams, or which have become displaced by waves and by undertow (Fig. 2b).

Displacement by Turbidity Currents

The environmental mixing of shallow-water benthonic Foraminifera into deeper water was cited by Phleger (1951) as one of the phenomena best explained by the action of turbidity currents (fig. 4c). He cited the example of faunal mixing in the bottom sediments of the San Diego Trough where shoal and shallow-water Foraminifera were found at depths of from 400 to 600 fathoms; these included species of *Cassidulina*, *Buliminella*, and *Discorbis*. Natland and Kuenen (1951) also described a similar situation in the Lower Pliocene Repetto Formation of the Ventura Basin. In this instance, species of *Elphidium* which normally range from the shore to depths of 300 feet were found in association with species of Foraminifera whose range in depth is from 4000 to 5000 feet and deeper. In discussing the sediments of the West Cortez Bank off the California coast, Emery and Rittenberg (1952) describe a core of coarse sand at a depth of 5784 feet containing a foraminiferal fauna characteristic of the Cortez Bank which is less than 500 feet in depth. Phleger (1951) also cites the evidences of displaced foraminiferal faunas in the bottom sediments of the Sigsbee Deep in the Gulf of Mexico, where cores from depths of 12,000 feet contain abundant species which are now restricted to waters less than 300 feet deep. In discussing the effects of temperature zonation on the Miocene to Recent Foraminifera and ostracodes in deep basins off the California Coast, Crouch (1952) describes many instances of samples from great depths which contain reworked and displaced shallow-water species. Many other examples exist of the displacement of shallow-water microfossils which have apparently been displaced into deeper water by the action of turbidity currents.

Displacement by Streams

Running water plays an important role in the displacement of microfossils. The principal role of streams in displacement is twofold: (1) reworking of older microfossils into younger horizons (redeposition), and (2) lateral displacement of indigenous faunas, (environmental mixing). The most common type of reworking is the transfer, by way of the stream, of weathered-out microfossils from older marine horizons into younger ones (fig. 5).

In the Mississippi River drainage system, the streams flow over progressively younger fossiliferous strata en route to the Gulf of Mexico, and many examples exist of the redeposition of late Paleozoic, Mesozoic, and Early Cenozoic microfossils into marine sediments since Oligocene time (fig. 6). Howe (1956, personal communication) described to the writer his observations of the Red River in spring flood in southern Louisiana, in which the turbid waters were found to contain numerous specimens of *Gümbelina*, *Globotruncana*, and *Inoceramus* prisms floating on the surface of the water enroute to the Gulf of Mexico. Barker (1956, personal communication) has shown the writer samples of sand from a bar in the Brazos River of Texas, which contains a mixture of modern charophytes, nonmarine ostracodes (*Candona*, *Cypris*), the common marine ostracodes *Cytheridea* and *Paracypris*, and the common Upper Cretaceous Foraminifera *Gümbelina*, *Globotruncana*, as well as Upper Cretaceous species of *Anomalina*. The same sample also contained Miocene-Pliocene species of *Nodosaria* and *Ceratobulimina*. The source beds for the reworked Upper Cretaceous forms in both of the above instances are in southern Oklahoma and northeast Texas (fig. 6).

Peck (1956, personal communication) reported to this writer that the Pleistocene loess along the Missouri River in central

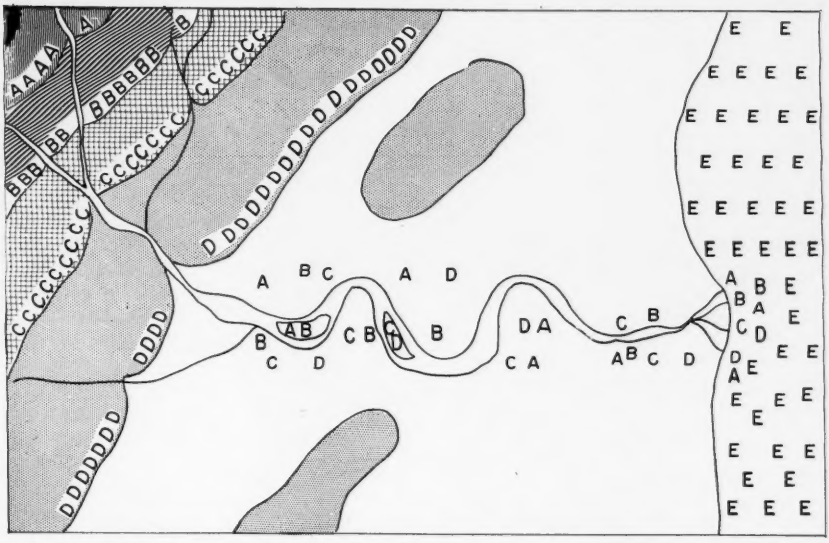

FIG. 5.—Redeposition by major stream draining an area of various fossiliferous outcrops; microfossils may be reworked into sediments of the channel, flood plain, delta, lake, or the ocean.

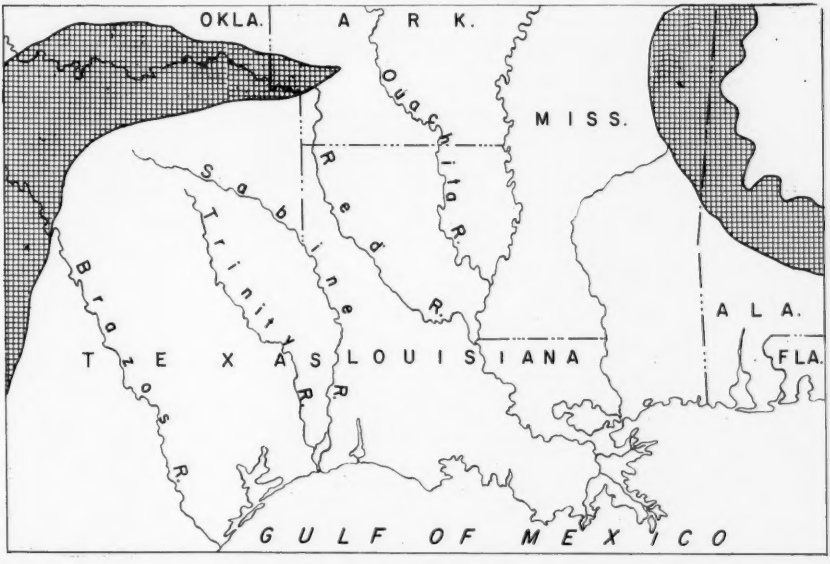

FIG. 6.—Map of a portion of the U. S. Gulf Coast showing relationship of fossiliferous Cretaceous outcrops to the streams redepositing Cretaceous microfossils in the Gulf of Mexico.

Missouri contains silt lenses rich in Cretaceous Foraminifera showing little or no signs of wear.

Numerous examples exist of the transportation of older marine microfossils into lacustrine environments. Hedberg (1956, personal communication) noted that the nonmarine Tertiary strata of the middle Magdalena valley in Colombia contain several zones of detrital Cretaceous Foraminifera including *Siphogenerinoides* and *Bulimina*. The occurrence of these "detrital" forms in well-defined zones enabled him to correlate the continental lacustrine beds, since the zones of Foraminifera apparently marked periods of active uplift and erosion of highly fossiliferous Cretaceous strata in the mountains west of the area.

Carrozzi (1955, personal communication) has described to the writer the abundance of upper Cretaceous *Globotruncana* in the bottom sediments of modern Lake Geneva, which have been washed in by streams flowing over exposed Cretaceous fossil zones in the surrounding mountains.

Hedberg (1956, personal communication) has also reported to the present writer that Recent sediments on the bottom of Lake Maracaibo in western Venezuela contain abundant Eocene arenaceous Foraminifera derived from nearby exposures.

The writer has observed Tertiary nonmarine ostracodes from the Salt Lake Group reworked into the Pleistocene sediments of Lake Bonneville on the south side of the Raft River mountains in northwestern Utah. The Pennsylvanian Oquirrh formation is exposed in the locale, with the Tertiary lake beds flanking it. Small intermittent streams flowing out of the Raft River Mountains transported both the oolites of the Oquirrh and the ostracodes of the Salt Lake Group to the shore of Lake Bonneville.

The Wanship formation, of uppermost Upper Cretaceous age in northeastern Utah, is a complex of fluvial sediments, primarily channel sands, floodplain siltstones with abundant plant remains and thin coals, which probably represents a fluvio-lacustrine and somewhat lagoonal environment. It overlies the marine Frontier Formation, which contains a number of zones of abundant Foraminifera. Lankford (1953) found in the Wanship a number of worn, rounded specimens of Foraminifera reworked from the Frontier into the lower portion of the Wanship, and was able to determine the amount of post-Frontier, pre-Wanship erosion by calculating the thickness of sediment removed from the Frontier down to the uppermost horizon of Foraminifera.

Displacement by Action of Ground Water

The solvent action of ground water and descending vadose water can accomplish the type of displacement known as the stratigraphic leak. The downward displacement of younger microfossils into solution cavities and joints in older limestones by marine transgression has been previously discussed. Branson and Mehl (1940) have described several cases in which conodonts have been displaced downward by the action of ground water (fig. 7). Descent of surface waters through mantle rock containing microfossils may transport such fossils into limestone caverns and sinks, thus burying younger fossils in older sediments. One such occurrence of this type is in exposures of Niagaran dolomite in the Elmhurst quarry near Chicago. The joints and bedding planes of the Niagaran contain Devonian and Lower Mississippian conodonts and fish teeth (Branson, C.C., personal communication).

Ground water can also produce stratigraphic leaks by intrastratal solution of thin fossil-bearing limestones in a shale sequence (fig. 7b).

Displacement by Wind Action

Wind displacement of microfossils is of three types: (1) incorporation of weathered-out older fossils into younger dunes migrating across a fossiliferous exposure (reworking), (2) formation of dunes made up of accumulations of organic remains on beaches of the ocean and of large lakes (environmental mixing), (fig. 8), and (3) incorporation of small microfossils such as spores, pollens, and diatoms into the suspension load and redeposition in dust deposits.

In the first case, Grabau (1913, p. 573–578) describes the movement of dunes of pure quartz sand across the floor of the Libyan desert. They eventually migrate across a portion of the desert floor underlain by fossiliferous Upper Cretaceous and

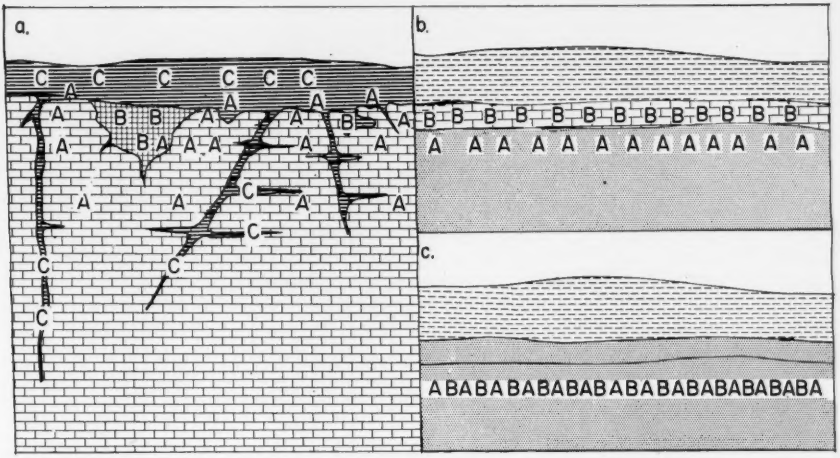

FIG. 7.—Displacement by ground water. a. Stratigraphic leak from a younger fossiliferous unit into solution cavities, pits, and bedding planes in an older limestone at an unconformity; b and c. stratigraphic leak produced by intrastratal solution of thin fossiliferous limestone in a shale sequence.

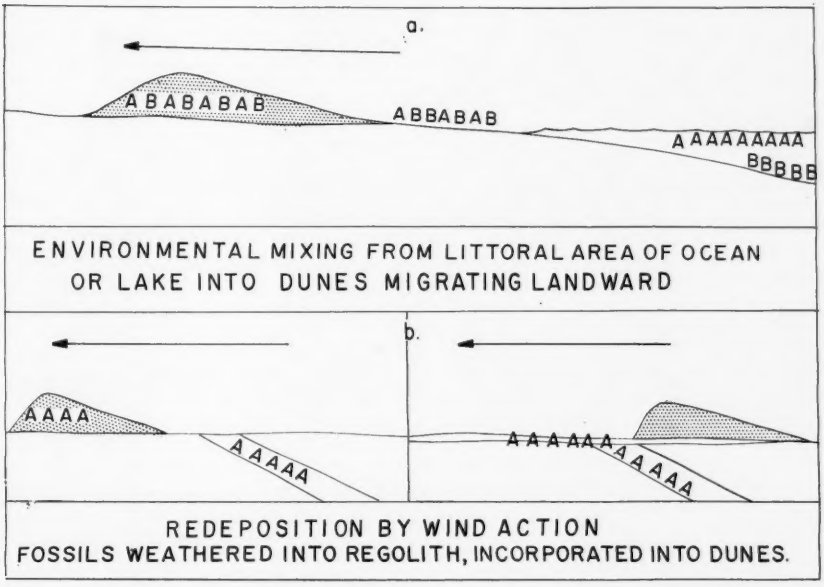

FIG. 8.—Displacement by wind action. a. environmental mixing from littoral area of ocean or lake into dunes migrating landward; b. weathered-out microfossils incorporated into migrating dune (sequence of events and wind direction from right to left).

Lower Tertiary strata, and the weathered-out microfossils, principally Foraminifera, are incorporated into the dunes (fig 8b).

Many examples exist of the incorporation of microfossils and fragments of larger fossils into dunes formed landward from the beaches of the ocean and of large lakes (figure 8a). Among the best-known examples are the dunes of the Dog's Bay area on the southwest coast of Ireland, near Galway. Shallow-water benthonic Foraminifera, including many species of Miliolidae, and the abundant planktonic form *Truncatulina lobatula* are carried into Dog's Bay and nearby Gortch Bay by surface drift. High tides spread out the tests on a gently sloping beach. The wind forms dunes of this material which includes ostracodes and shell fragments, and the material travels several miles inland across the isthmus (Grabau, 1913).

Evans (1900) describes a calcarenite, the Junagarh Limestone lying above the Deccan trap in the Kathiawar Peninsula in western India, which is composed of Recent shallow-water Foraminifera and coral fragments. The cross-bedded limestone is about 30 miles from the sea, and consists of worn and polished tests of *Amphistegina lessoni, Pulvinulina, Operculina, Rotalia, Miliolina,* and abundant ostracode fragments. The Junagarh is strongly cross-bedded in many directions, and is undoubtedly a dune deposit.

The general area surrounding the eastern Mediterranean and the Arabian and Red Seas contains many areas composed of dunes of calcarenite made up primarily of the tests of Foraminifera; fragments of the large orbitoids are quite common, and on the coast of the Arabian Sea there are many dunes composed entirely of Miliolidae.

The 500-foot Montpelier Limestone of Jamaica is almost entirely composed of whole and fragmental tests of Foraminifera. The beach and dune sands of the Virgin Islands and of Bermuda are commonly a microcoquina or calcarenite composed primarily of Foraminifera, ostracodes, and mollusks.

The present writer has described a great series of gypsum-oolite dunes occurring on the eastern margin of the Great Salt Lake Desert of Utah which contain quite a number of ostracodes and gastropod fragments derived from the huge playa which in early Recent time occupied the desert (Jones, 1954). Recent work by the writer on the sediments of Danger Cave, an archaeological site in the Pilot Range on the Utah-Nevada line, shows that the mouth of the cave area is blocked with dunes of oolites, algal fragments, and abundant ostracodes from this same playa lake.

The wind dispersal of spores and pollens from the source plants into such varied environments as the flood plains of streams, lakes, lagoons, and the nearshore environments of the oceans is an excellent example of environmental mixing which has been put to significant use in both stratigraphic and paleoecologic work (fig. 9). The relative abundance of the spores in various samples makes possible the determination of the source area, and the wide dispersal of similar forms makes possible the correlation of marine with nonmarine strata.

Displacement of Microfossils by Organisms

Redeposition, stratigraphic leaks, and environmental mixing of microfossils are frequently accomplished by the action of organisms. Burrowing forms including insects, crustaceans, worms, and various rodents accomplish both redeposition and downward reworking of younger fossils into older horizons (fig. 10). In the Hatchitigbee Anticline area of Florida microfossils of the Lisbon Formation have been displaced downward as much as three feet into the underlying Tallahatta Formation by the burrowing action of crabs (Branson, C.C., 1956, personal communication), and in the Oklahoma-Texas Panhandle gopher burrows have carried snails and pollens of Pleistocene age several feet downward into the underlying Tertiary Ogallala Formation (Branson, C.C., 1956, personal communication). Also, in the continental Tertiary Bridger Formation of southwestern Wyoming, the writer has observed large ant hills whose component fragments contain small teeth and other bone fragments brought up from the fossiliferous Eocene beds below as the ants expand their subterranean burrows (fig. 10b).

Migratory waterfowl play a somewhat significant part in environmental mixing of fossils. As they travel on their flyways they land in such varied aquatic environments as the stream, flood plain lake, coastal and in-

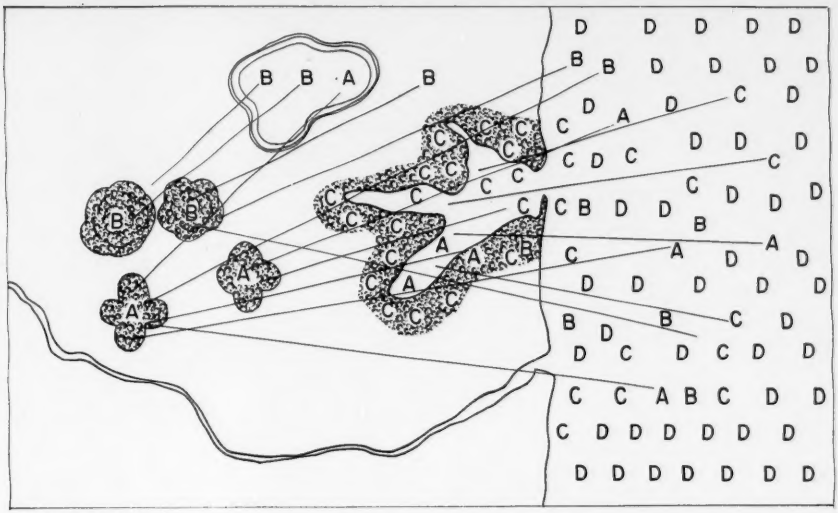

FIG. 9.—Environmental mixing by means of wind dispersal of airborne spores and pollens into lacustrine, lagoonal, and nearshore marine environments.

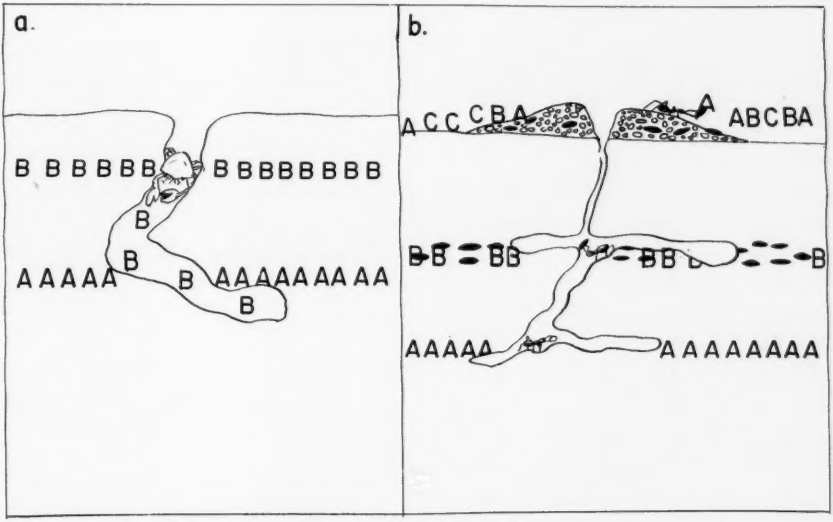

FIG. 10.—Displacement by organisms: a. stratigraphic leak produced by action of burrowing organism; b. redeposition produced by action of burrowing organism.

land lake, open marine waters, and the shallow, restricted environments of bays and lagoons (fig. 11). Their feet and plumage become hosts for a variety of planktonic and nektonic microorganisms including Foraminifera, limnetic ostracodes, diatoms, and

algae. Benthonic microorganisms may be taken into the digestive system of the birds and excreted in quite another environment. Several species of ostracodes have been known to extend their northward range from South America into North America within a comparatively few years primarily by "hitch-hiking" from lake to lake on the plumage and feet of migratory waterfowl.

Displacement by Glaciers

In considering this form of displacement, the incorporation of erratic boulders, cobbles, and pebbles of fossiliferous older strata into moraines will not be considered as true diaplacement. Several examples exist, however, of the incorporation of weathered-out microfossils from older regoliths into the glacial drift and subsequent dispersal from the drift into various environments (fig. 12a).

For example, many micropaleontologists suggest that the Pleistocene shallow-water

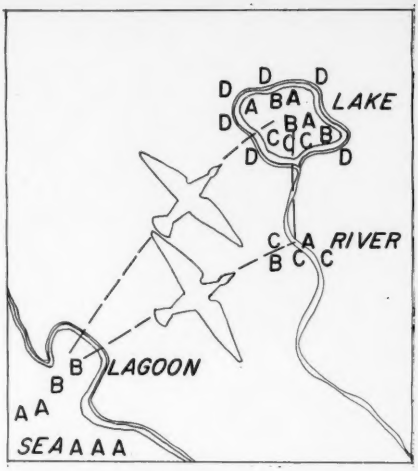

FIG. 11.—Environmental mixing by action of migratory waterfowl (organisms on plumage, feet, in excreta of birds).

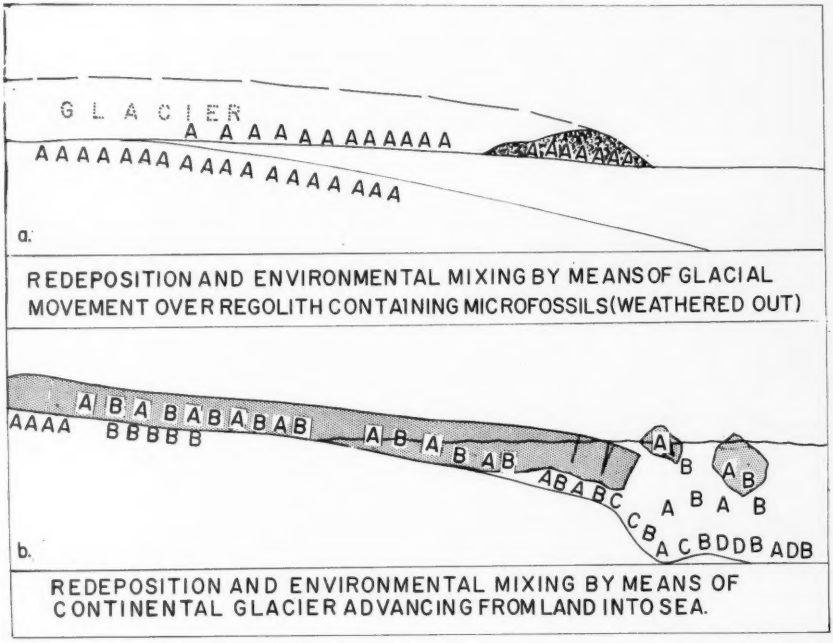
GLACIER
a.
REDEPOSITION AND ENVIRONMENTAL MIXING BY MEANS OF GLACIAL MOVEMENT OVER REGOLITH CONTAINING MICROFOSSILS (WEATHERED OUT)
b.
REDEPOSITION AND ENVIRONMENTAL MIXING BY MEANS OF CONTINENTAL GLACIER ADVANCING FROM LAND INTO SEA.

FIG. 12.—Displacement by glacial ice: a. redeposition and environmental mixing by means of glacial movement over regolith containing weathered-out microfossils; b. redeposition and environmental mixing by means of continental glacier advancing from land into sea.

Foraminifera reported by Ericson, Ewing, and Heezen (1952) from the deep waters of the North Atlantic may have been picked up from nearshore by late Wisconsin glaciers and rafted into the deep waters (fig. 12b) (Rainwater, 1956, personal communication).

Kaye (1952) cites two examples of the redeposition of Cretaceous and Paleocene Foraminifera by incorporation into glacial drift. In one instance the 100-mesh sieve fraction of a glacial drift near Froid, Montana, was found to contain abundant Upper Cretaceous *Globigerina* which showed little or no breakage. The source rock for the foraminiferal tests is a series of exposures in the foothills of the Canadian Rockies about 130 miles north of the exposure of the drift. In another instance Foraminifera from the underlying Cannonball Formation were found in fine fractions of a blue-gray Pleistocene till exposed one-half mile southeast of Velva, North Dakota.

Hough (1934) has described a most unusual case of redeposition in which glaciers, slope wash, and lakes were involved. The tap water in the paleontology laboratories of Walker Museum at the University of Chicago was found to contain Devonian spores, which had been incorporated into the Wisconsin drift in the Chicago area, washed into Lake Michigan, and taken from the lake into the municipal water system. Core samples of Recent Lake Michigan bottom clays were found to contain the same type of remains.

Displacement by Other Natural Processes

In addition to the mechanisms previously described, there are examples of displacement of microfossils by such miscellaneous processes as intrusion, or "squeeze-up" of older sediments into younger sediments during compaction, the action of mud volcanoes near beaches, and salt dome intrusions of older strata into younger submarine sediments with subsequent submarine wave and current erosion and redeposition (fig. 4a).

ARTIFICIAL DISPLACEMENT (CONTAMINATION)

Contamination of samples collected for purposes of micropaleontological analysis is at times a cause of serious misinterpretation of faunal content. Both surface and subsurface samples can become contaminated in the field and in the laboratory.

Field Contamination of Surface Samples

Material collected in the field as surface samples can become contaminated with undesired microfossils from (1) improperly cleaned implements such as picks, shovels, and other tools used in digging or breaking off the samples from the outcrop; (2) surface contamination of outcrop samples by airborne dusts containing pollens, spores, and similar small organic remains; (3) slope wash of higher, softer fossiliferous materials down over the surface of a lower outcrop.

Contamination of Subsurface Samples

Contamination of upper horizons into lower samples is likely if improper augering of shallow test holes is done. Most of the serious contamination, however, comes from ditch samples obtained during rotary drilling operations. The problem is not quite so serious in those subsurface sections containing numerous horizons of extremely abundant microfossils, such as those in the Tertiary of the Gulf Coast and California. In many of the Paleozoic and Mesozoic sections penetrated by the drill, however, the numbers of microfossils encountered are considerably less, and the results of contaminations can seriously affect interpretation of data obtained from micropaleontological analysis. Contamination of samples during rotary drilling operations is usually caused by: (1) separation of the fossils from the matrix during drilling and circulation of mud, rendering impossible the association of the fossil with its containing lithology, (2) recirculation of fossils from the mud pits back into the circulation system, (3) re-use of drilling mud from one well to another without proper screening and removal of old cuttings, (4) accumulation of fossils and fragments on the bottom of the hole during periods of low pump pressure, then reagitation and displacement by subsequent increases in mud stream pressures and velocities, (5) mechanical size-sorting of fossils and fragments by settling back through the ascending mud stream at varying densities and velocities.

Contamination of Samples in the Laboratory

The preparation and separation of samples in the laboratory affords many opportunities for contamination, most of which can be avoided by proper care. Common sources of laboratory contamination are: (1) air contamination of samples by such dust particles as diatoms, spores, and pollens, or by dust from dry sieving of concentrates, (3) accidental spilling of samples, and (4) contamination due to improper cleaning of laboratory vessels and equipment including beakers, mortars, pestles, screen sieves, brushes, and stirring rods.

CRITERIA FOR RECOGNITION OF DISPLACED MICROFOSSILS

The following criteria for recognition of displaced microfossils are suggested by the writer, based upon an earlier listing (Jones, 1956) and upon subsequent studies of displaced faunas:

1.—Abnormally high percentages of fragmentary microfossils or of highly ornamented tests whose spines, nodes, ridges, or other ornamentation may be partially or entirely worn off suggest strongly that the tests have peen transported. This is particularly true of larger microfossils in the size range of granules and coarse sand.

2.—The abundance of dissociated parts or skeletal fragments but absence of articulated portions or complete remains of such forms as echinoids and crinoids, may suggest displacement.

3.—If the largest microfossils in the sediment are no larger than the largest inorganic particles, of if the average particle size distribution of the microfauna closely resembles that of the containing sediment, the chances are that the fauna was introduced with the sediment.

4.—The occurrence of specimens of differing color, texture, or mineral composition within the same species suggests that some of the specimens may be displaced.

5.—The absence of normal growth stage series and of immature forms of most of the species strongly suggests some type of particle size sorting, indicating displacement of the fauna.

6.—In the case of assemblages consisting of large numbers of arenaceous Foraminifera, obvious differences in the degree of distortion or compaction of the specimens, suggests that part of the fauna may be displaced.

7.—Bedding plane surfaces may on occasion exhibit large numbers of such elongate microfossils as fusulinid tests which show a preferred orientation, their long axes all parallel. This may indicate reworking or displacement laterally.

8.—If mixing of faunas is suspected, it is probable that those forms exhibiting the highest degree of sphericity and buoyancy have been introduced into the assemblage.

Recognition of stratigraphically displaced microfossils necessitates a thorough knowledge of normal stratigraphic ranges and sequences of microfaunas. The greater the stratigraphic interval represented by the entire fauna, the more readily recognizable is the displaced element.

CONCLUSIONS

From this brief review of the natural and artificial displacement of microfossils, certain conclusions may be drawn:

1.—Microfossils, because of their small size, are particularly susceptible to displacement, either horizontal or vertical, after deposition and before final entombment.

2.—Redeposition, or the displacement of older fossils into younger zones, is more common than the stratigraphic leak.

3.—Environmental mixing, intracontinental, intramarine, from continental into marine, and vice versa, is also a fairly common phenomenon.

4.—Horizontal and vertical displacement are both accomplished by such natural agents as waves and currents, streams, turbidity currents, ground water, gravity, glacial ice, wind, and by various organisms.

5.—Artificial displacement or contamination of samples both in the field and in the laboratory can produce serious complications in the interpretation of micropaleontological data.

6.—Displacement should be expected at unconformities, at contacts or facies changes between marine and non-marine sedimentary units, and in areas known to be adjacent to ancient shorelines during various intervals of geologic time.

ACKNOWLEDGEMENTS

The writer wishes to acknowledge the excellent cooperation of his professional colleagues who furnished most of the examples of displacement discussed in this paper; these have been acknowledged as personal communications in the text, rather than in the list of references. These colleagues include H.D. Hedberg, H.N. Coryell, R.L. Denham, H.V. Howe, C.C. Branson, C. Rainwater, R.W. Barker, R.E. Peck, A. Carrozzi, and O.L. Bandy.

REFERENCES

BANDY, O. L., 1952, Road log, S.E.P.M. field trip, unit #1, Palos Verdes Hills and San Pedro: Field Trip Guidebook, A.A.P.G.-S.E.P.M.-S.E.G., joint annual meeting, Los Angeles, California, p. 9–13.

BRANSON, E. B., AND MEHL, M. G., 1940, Recognition and interpretation of mixed conodont faunas: Denison Univ. Sci. Lab. Bull., v. 35, p. 195–209.

CARRIGY, M. A., 1956, Organic sedimentation in Warnbro Sound, Western Australia: Jour. Sedimentary Petrology, v. 26, p. 228–239.

CROUCH, R. W., 1952, Significance of temperature on Foraminifera from deep basins off the California coast: Am. Assoc. Petroleum Geologists Bull., v. 36, p. 807–843.

———, 1954, Paleontology and paleoecology of the San Pedro shelf and vicinity: Jour. Sedimentary Petrology, v. 21, p. 182–190.

ELLISON, S. P., JR., 1951, Microfossils as environmental indicators in marine shales: Jour. Sedimentary Petrology, v. 21, p. 214–225.

EMERY, K. O. AND RITTENBERG, S. C., 1952, California basin sediments and the origin of oil: Am. Assoc. Petroleum Geologists Bull. v. 36, p. 743–744.

ERICSON, D. B., EWING, M. AND HEEZEN, B. C., 1952, Turbidity currents and sediments in the North Atlantic: Am. Assoc. Petroleum Geologists Bull., v. 36, p. 489–511.

EVANS, J. W., 1900, Mechanically formed limestones from Junagarh (Kathiawar) and other localities: Geol. Soc. London, Quart. Jour. v. 56, p. 559–583, 588–589.

GRABAU, A. W., 1913, Principles of stratigraphy: A. G. Seiler and Co., New York, 1185. p.

HOUGH, J. L., 1934, Redeposition of microscopic Devonian plant fossils: Jour. Geology, v. 42, p. 646–648.

JONES, D. J., 1954, Gypsum-oolite dunes, Great Salt Lake Desert, Utah: Am. Assoc. Petroleum Geologists Bull., v. 37, p. 2530–2538.

———, 1956 Introduction to microfossils. Haper and Brothers, New York, 406 p.

KAYE, C. A., 1952, Foraminifera in glacial till from northeastern Montana: Geol. Soc. America Bull., v. 63, p. 881.

LANKFORD, R. R., 1953, Microfossils of the Wanship, *in*, Microfossils of the Upper Cretaceous of northeastern Utah and southwestern Wyoming: Utah Geological and Mineralogical Survey Bull. 47, p. 21–22.

NATLAND, M. L., 1933, The temperature and depth distribution of some Recent and fossil Foraminifera on the southern California coast: Bull. Scripps Inst. Oceanography, Tech. Ser., v. 3, p. 225–230.

NATLAND, M. L., AND KUENEN, PH., 1951, Sedimentary history of the Ventura Basin, California, and the action of turbidity currents: *in*, Turbidity currents and transportation of coarse sediments into deep water: Soc. Econ. Paleont. Mineralog., Special Publication 2, p. 76–107.

PHLEGER, F. B., 1951, Displaced Foraminifera faunas: *in* Turbidity currents and transportation of coarse sediments into deep water: Soc. Econ. Paleont. Mineralog., Special Publication 2, p. 66–75.

REVELLE, R. W., AND SHEPARD, F. M., 1955, Sediments off the California coast: *in*, Recent marine sediments: Soc. Econ. Paleont. Mineralog. Special Publication nol 4. p. 245–282.

SHROCK, R. R., AND TWENHOFEL, W. H., 1953, Principles of invertebrate paleontology: McGraw-Hill Book Company, Inc., New York, 782 pp.

JOURNAL OF SEDIMENTARY PETROLOGY, VOL. 28, NO. PP. 468–481
FIGS. 1–3, DECEMBER, 1958

TECHNIQUES IN SEDIMENTARY GEOCHEMISTRY: (1) SEPARATION OF THE DETRITAL AND NON-DETRITAL FRACTIONS OF LIMESTONES[1]

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ABSTRACT

A method is outlined whereby the contents of ten trace elements in the non-detrital fraction of limestones can be determined spectrographically down to values of the order of 0.05 ppm. For five other elements the method is useful but less sensitive. The method is based on the mixed precipitants technique of Mitchell and Scott (1947) and Heggen and Strock (1953) modified to satisfy the requirements of investigations in sedimentary geochemistry.

INTRODUCTION

Geochemical investigations may determine the distribution of selected elements through a wide range of geological materials (for example, Shaw, 1952a, b), or alternatively the contents of as many elements as possible may be determined in a number of related rocks (Wager and Mitchell, 1943, 1951; Nockolds and Mitchell, 1948; and Nockolds and Allen, 1953, 1954, 1956).

The techniques for the two types of investigation are sharply contrasted. The former requires methods selective for the element studied; the latter requires methods enabling as many elements as possible to be determined in the minimum number of operations. As has long been realised, spectrographic techniques are particularly appropriate for this second type of investigation.

In the study of sedimentary rocks the content of trace elements may often be below the limit of detection by normal spectrographic methods. In many cases, however, a marked concentration of several trace elements present may be effected by the use of a suitable precipitation technique if the rock can be brought into solution. Thus a combined precipitation-spectrographic technique is distinctly more sensitive for certain elements than a direct spectrographic analysis of the sample.

In certain respects geochemical investigations of sedimentary rocks involve greater difficulties than are encountered in studies of igneous rocks. Krynine (1948) pointed out that sedimentary rocks may be regarded as a mixture of material carried into the basin of deposition in the solid state and material entering the basin of deposition in solution. The former will be referred to here as *detrital* material. Since the latter may become incorporated into the sediment through a variety of processes the term *non-detrital* material will be applied to it. This term in no way implies any definite process of extraction from solution into the sediment. While the trace elements present in igneous rocks may reasonably be regarded as having been present in the magma from which the igneous rock crystallised, no such simple hypothesis can be utilized in sedimentary studies. Trace elements contained in sedimentary rocks may be of detrital or non-detrial origin. Thus for a full understanding of the geochemistry of sedimentary rocks it is insufficient to determine only the trace element contents of the total rocks; it is necessary to determine the detrital and non-detrital contributions of any given element to the total composition of the rock.

The fine grain and intimate admixture of the minerals of many shales, marls, and related rocks makes inapplicable the techniques of mineral separation used in studies of igneous rocks, and at present selective chemical attack on the rocks appears a more hopeful line of enquiry. Many impure limestones, for example, can be considered to contain two distinct fractions, an essentially carbonate fraction, such as $CaCO_3$ or $FeCO_3$ of non-detrital origin, and a detrital fraction made up essentially of silicates, clay minerals or quartz. A weak acid attack on the rock will liberate into solution those ele-

[1] Manuscript received April 18, 1958.

ments in the carbonate fraction and those which can be leached from the detrital fraction, for example by ion-exchange, but will leave in the residue those elements occupying structural positions in the silicates. While some separation of detrital and non-detrital trace elements is thus effected it is clear that certain non-detritals may be left in the unattacked residue (original colloidal material that has subsequently recrystallised to acid-resistant minerals, non-detrital sulphides, for example) and consideration must be given to this in interpretation of results. Filtration and washing of the residue from such an acid attack effects a separation of those elements in the acid soluble fraction from the remainder of the rock.

Evaporation of the acid solution would permit the elements in this fraction to be collected as a mixture of salts. This mixture would be largely calcium and magnesium salts (if the acid soluble fraction had been obtained by attack on limestones) and, as later results (table 4) will show, the content of trace elements would frequently be below the limit of sensitivity of normal spectrographic methods. It is desirable, therefore, to precipitate the trace elements from the acid solution selectively, leaving the calcium and magnesium in solution. This can be done by the use of organic reagents.

Organic reagents have long been used in inorganic analysis particularly in the evolution of methods specific to one element. Some reagents lack the necessary specific character and complex a considerable number of inorganic ions. These reagents can be applied to a problem such as the one considered here when, within certain limits, the less specific their character the better. If D.C. arc spectrographic analysis is to be applied, it is clearly desirable that the organic reagents used should involve a precipitation rather than an extraction procedure since the latter would involve evaporation of the resulting solutions and collection of their contained elements into a solid base.

The value of 8-hydroxyquinoline as an organic complexing reagent was early realised by Scott and Mitchell (1943) who developed a technique using this reagent only, aluminium and iron quinolates acting as carrier precipitates. The incomplete precipitation of chromium, vanadium, silver, tin, lead, germanium, beryllium, and cadmium by this reagent led to the development (Mitchell and Scott, 1947) of the mixed precipitants technique using the combined effects of 8-hydroxyquinoline, tannin, and thionalide. The precipitation of silver, tin, and lead is probable as thionalates but the scavenging effect of the tannin is probably significant in rendering the precipitations quantitative, especially for chromium, vanadium, and beryllium.

Other organic reagents possessing potentialities for investigations of this type are ammonium nitrosodiphenylhydroxylamine (cupferron), anthranilic acid, and 5-bromo-2- aminobenzoic acid. Details of their reactions are given by Flagg (1948).

DETAILS OF PROCEDURE

Chemical Procedure

The chemical technique adopted in this work is essentially the mixed precipitants procedure outlined by Heggen and Strock (1953) and based on that originally developed by Mitchell and Scott (1947). This combination of organic complexing reagents has been found to precipitate silver, aluminium, bismuth, cadmium, cobalt, chromium, copper, iron, gallium, germanium, indium, molybdenum, beryllium, nickel, lead, tin, titanium, vanadium, and zinc quantitatively under the conditions used. Elements other than those listed are precipitated, but have not at present been studied quantitatively. Calcium and magnesium are not precipitated if careful attention is paid to operating conditions, and hence when the technique is applied to the analysis of the acid soluble fraction of limestones, a notable concentration of other elements is achieved in the collected precipitate. In the determination of the trace element content of the non-detrital fraction of a limestone, the primary attack is by 25% (by volume) acetic acid. Ray, Gault and Dodd (1957) have demonstrated that this acid dissolves the carbonates but will not destroy the clay mineral lattices. The volume of acid used depends on the weight of rock taken and is normally 100 ml for 10–12 gm of rock. However, if it is thought that the precipitate may be small, as would be expected in the case of a very pure limestone, a larger sample and consequently a greater volume of acid may be taken. After agitation and leaving overnight, the insolu-

ble residue is filtered off and thoroughly washed with dilute acetic acid. To the filtrate is then added a 5% solution of 8-hydroxyquinoline in 2N acetic acid. Heggen and Strock (1953) report that 10 ml is sufficient, but since the precipitates in rock analysis are liable to be of appreciable size, 15–20 ml of this precipitant is better. The sample is then brought to pH 1.8 by adding hydrochloric acid. It was found that the use of acetic acid as the solvent made it necessary to add hydrochloric acid at this stage since the pH was invariably above 1.8. A green colour at pH 1.8–1.9 is indicative of the presence of iron, presumably in the form of iron quinolate. Forty-five ml of 2N ammonium acetate are then added and the pH adjusted to 5.2 by the addition of dilute ammonium hydroxide. A pH meter with extension electrodes is used for these determinations because the pH of 5.2, in particular, is critical. If the pH is below 5.2, chromium, nickel, lead, and tin are incompletely precipitated, while at a higher pH calcium and magnesium are precipitated. Two ml of a freshly prepared 10% solution of tannic acid in 2N ammonium acetate are then added and stirred, after which, 2 ml of a 1% solution of thionalide in glacial acetic acid is added. After stirring, ammonia equivalent to the 2 ml of glacial acetic acid is added, the quantity having been previously determined by titration with bromthymol blue as indicator.

The solution, after further stirring, is left to stand overnight and is then filtered through a Whatman No. 40 filter paper, using suction. The precipitate is washed thoroughly with a dilute solution of 8-hydroxyquinoline in distilled water, buffered to a pH of 5.2 with ammonium acetate. The precipitate, in an ignited, weighed, porcelain crucible, is then slowly heated to 450°C in an electric muffle furnace, at which temperature it is ashed overnight. The amount of precipitate from rock analysis is liable to be quite appreciable, consequently carrier precipitates are seldom necessary. If, however, it is thought that the amount of precipitate is likely to be very small, a carrier precipitate of iron or aluminium oxide can be added (Mitchell and Scott, 1948). The chief reason for the omission of indium, used as a carrier precipitate and internal standard by Heggen and Strock (1953) was the desire to analyse for this element, its quantitative precipitation by the technique making this possible.

Spectrographic Procedure

General techniques.—The ash is cooled, weighed, and transferred to a mortar where, if of insufficient amount for the necessary determinations to be made, a weighed amount of iron oxide or aluminium oxide is added and thoroughly mixed with the precipitate. The mixture is then split into two fractions. To one fraction a carbon-palladium mixture (containing 1000 ppm Pd) is added in the proportion one part of ash fraction to two parts carbon-palladium mixture; this charge is used for the determination of the involatile elements. To the other fraction sodium carbonate containing 1000 ppm thallium is added in the proportion four parts of ash fraction to one part Na_2CO_3-Tl mixture to produce the charge used for the determination of volatile elements. Sodium carbonate, as a buffer, satisfactorily reduces CN emission and enables readings to be made on certain sensitive lines which would otherwise be obliterated by CN bands. The possibility of introducing both internal standards with the carbon buffer was considered, the CN emission to be suppressed by arcing in a CO_2 atmosphere with a jet of the same gas surrounding the arc. Investigation showed that CN emission was not satisfactorily suppressed. Heggen and Strock (1953) used indium as internal standard, but our investigations on the volatility of this element and the more involatile elements precipitated, such as chromium and vanadium (fig. 1), have indicated that indium was less satisfactory than palladium as an internal standard for these elements.

The charges, prepared as described above, are placed in high quality carbon anodes accurately machined to the following dimensions: outside diameter 4.8 mm, crater internal diameter 3.2 mm, crater depth (cylindrical) 6.0 mm. Pointed cathodes are cut from the same high quality carbon rod. Anode excitation in a D.C. arc is used. Charges for the determination of involatile elements are pre-heated for approximately 10 seconds at 4–5 amps and then arced to completion at 7 amps. Charges for the determination of volatile elements are arced for 5 minutes in the Fe_2O_3 matrix and 7 minutes in the Al_2O_3 matrix at 4 amps. The

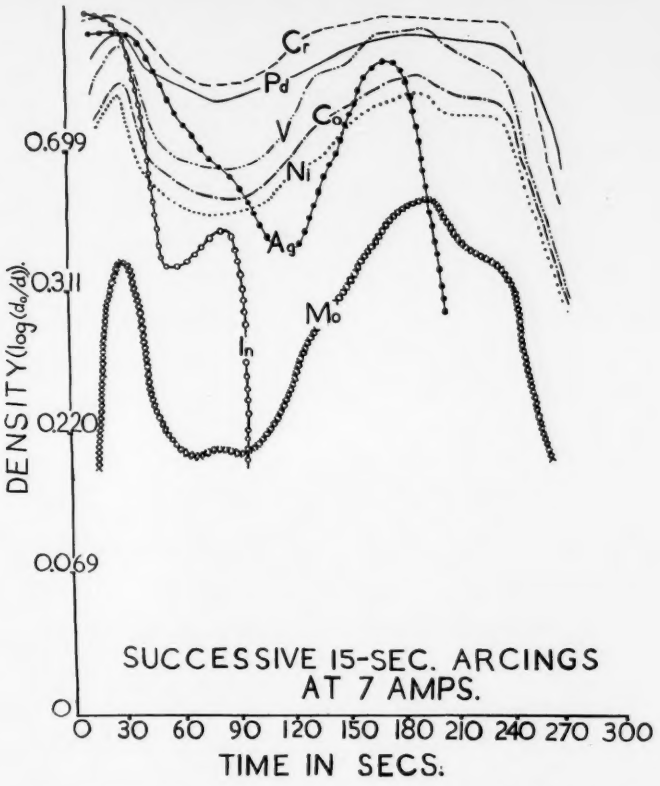

FIG. 1.—Volatility curves for the elements, chromium, vanadium, nickel, cobalt, silver, molybdenum, indium and palladium in an Fe_2O_3 matrix, arced at 7 amperes to completion.

plates are processed according to the makers' instructions and photometered on a Hilger non-recording microphotometer. Calibration curves are constructed from galvanometer readings using Seidel function[2]-millimetre graph paper, designed in this laboratory and prepared by J. Halden and Co. of Manchester, and background corrections applied where necessary (for details see Rushton and Nicholls, 1957). Table 1 shows the lines used over the wavelength range 2810Å–5000Å.

Standards for compilation of working curves.—Ashing, subsequent to the precipitation by organic complexing reagents, converts an originally organic precipitate to a mixture of oxides. Consequently, standards are prepared by straightforward dilution of a series of oxides of the elements known to be quantitatively precipitated by the technique. These standards are subsequently divided each into two portions to which appropriate buffers and internal standards are added as for analysis material.

[2] The Seidel function $\log \{(d_0/d) - 1\}$—where d_0 is the galvanometer reading for photometer beam transmitted through clear glass of photographic plate and d the reading for transmitted beam after passage through a spectral line—is frequently preferred to the density function, $\log d_0/d$, on account of the extended straight section of the characteristic curve produced.

TABLE 1.—*Data on wavelengths of lines used for trace element determinations*

Element	Wave length Å	Excitation potential	Other wave lengths	Remarks
Pd	3481.152	4.78 v.	—	Internal standard for involatile fraction.
Tl	3775.72	3.27 v.	—	Internal standard for volatile fraction.
Ni	3414.765	3.64 v.	3524.541 3492.956	Involatile; detection limit 3 ppm.
Co	3453.505	4.00 v.	3403.120	Involatile; detection to 1 ppm.
V	4379.238	3.12 v.	—	Involatile; detection to 1 ppm. Line used in Al_2O_3 matrix.
	3185.396	3.94 v.	—	Involatile; detection to 1 ppm. Line used in Fe_2O_3 matrix.
Cr	4254.346	2.90 v.	4274.803	Involatile; detection to 1 ppm.
Mo	3170.347	3.89 v.	3798.252 3902.963	Involatile; detection to 1 ppm. Interference precludes use of most sensitive line.
Ag	3280.683	3.75 v.	3382.891	Analysed better with the involatiles. Detection to <1 p.p.m. Self absorption at concentrations higher than 316 ppm.
Be	3130.416	3.94 v.	3131.072	Involatile; detection to <10 ppm. Wave length precludes use of most sensitive line.
Pb	4057.82	4.36 v.	3683.471	Volatile; detection limit ≏3 ppm.
Ga	4172.056	3.06 v.	4032.982	Volatile: detection to 1 ppm. Al_2O_3 base. Dectection to 10 p.p.m. Fe_2O_3 base.
In	4511.323	3.01 v.	3256.09	Volatile; detection to 1 ppm.
Ge	3039.064	4.94 v.	3269.494	Volatile; detection to <10 ppm. Self absorption probable at concentrations higher than 316 ppm.
Cu	3247.540	3.80 v.	3273.962	Volatile; detection to 1 ppm. General low slope due to contamination from carbons. Self absorption probable at concentrations higher than 316 ppm.
Bi	3067.716	4.02 v.	4722.552	Volatile; detection to 1 ppm. Fe_2O_3 base. Detection to 10 ppm. Al_2O_3 base.
Sn	3175.019	4.31 v.	3262.328 2839.989	Volatile; detection limit approximately 30 ppm.
Cd	3261.057	3.78 v.	3466.201	Volatile; detection limit approximately 30 ppm. Wave length precludes use of most sensitive line.
Zn	3345.020	7.75 v.	4810.534	Volatile; rather insensitive, detection limit <300 ppm. Wave length precludes use of most sensitive line.

Necessity for blank determinations. Important factors to be considered in work of this nature are the sources of contamination. The distilled water used both for making up solutions and for washing apparatus should be at least doubly distilled in glass or alter-

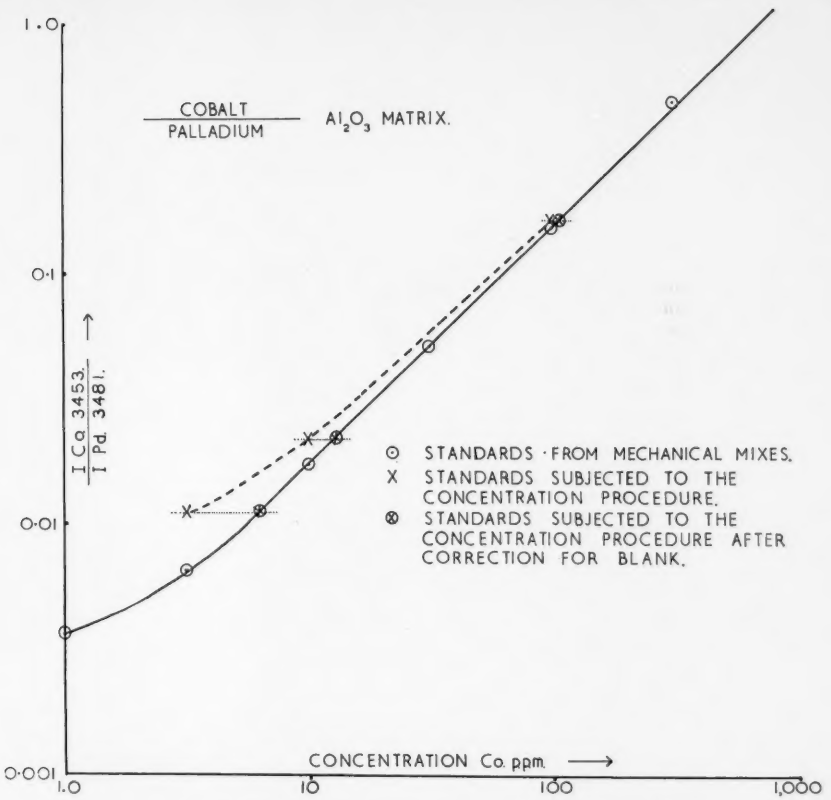

FIG. 2.—The cobalt working curve in an Al_2O_3 matrix: cobalt vs. palladium.

natively purified by passage through an ion exchange column. Reagents used must be of a high standard of purity and all glass-ware should be soaked in acid solution and thoroughly washed in the specially purified water before use. The cleaning agents used should contain no elements to be determined, thus precluding the use of the chromate-sulphuric acid cleaning agent. It is extremely important that blanks should be run with all samples. These should receive exactly the same amounts of acids, reagents, and water as the samples, the values derived for trace elements being subtracted from sample values. Heggen and Strock (1953) point out that blank values are usually lower when electrical heating apparatus rather than gas is used.

Extensive checks on the quantitative accuracy of the procedure were carried out be Heggen and Strock (1953) who treated a series of standard solutions to the precipitation procedure. Consequently only three standards were taken through the procedure, 100 ppm, 10 ppm, and 3.16 ppm. Figure 2 shows the cobalt working curve in an Al_2O_3 matrix. The values of intensity ratio for the standard at 100 ppm show close correspondence to those from mechanical mixtures, but in the lower part of the curve intensity ratios are higher for those samples which had been treated by the precipitation procedure. This may be attributed to contamination from the chemicals used in the

precipitation technique. Such contamination can be corrected by running blanks. Blank values on one run were: Ni 28 ppm, V 17.5 ppm, Cr 7.7 ppm, Pb 15 ppm, Cu 12.8 ppm, Co 3 ppm, Bi 1.1 ppm. Ag trace, Mo, Ti, Sn, Cd, Zn, In, and Ga are below the detection limit. Thus the Co contents of the three standards taken through the procedure should be corrected to 103 ppm, 13 ppm, and 6.16 ppm. The corrected working curve is plotted in figure 2 and coincides with the working curve compiled from the oxide standards. This indicates that precipitation is quantitative and that working curves can be prepared using oxide standards. It also emphasizes the need to run blanks with any series of samples being analysed and to make appropriate blank corrections.

Reproducibility of Results

Calculation of the amounts present in the soluble fraction of the rocks, from the determinations on the ashed concentrates is made by applying the formula

$$\text{Content of element } E \text{ in soluble fraction} = N \frac{X}{x} \cdot \frac{y}{Y}$$

where ashed diluted concentrate contains N ppm of an element E, x gm is the weight of ashed concentrate added to $X-x$ gm of dilutent material (Al_2O_3 or Fe_2O_3) to give X gm of analysis material. y gm is the total wt. of ashed concentrate obtained from Y gm of soluble fraction, where Y is the difference in weight of original limestone taken and the weight of residue left after acetic acid attack.

Table 2 presents the results of eight separate Cr determinations in the soluble fraction of the Jurassic limestone A.N.9 and standard deviations for the other elements.

The small number of determinations used implies that these standard deviations are only approximate.

TABLE 2.—*Reproducibility data for limestone A.N.9: Chromium*

ppm Cr.	Deviation	% deviation	(% deviation)²
0.35	−0.02	− 5.4	29
0.41	+0.04	+10.8	117
0.33 (5)	−0.03 (5)	− 9.5	90
0.32	−0.05	−13.5	182
0.34	−0.03	− 8.1	65
0.40 (5)	+0.03 (5)	+ 9.5	90
0.40	+0.03	+ 8.1	65
0.40	+0.03	+ 8.1	65

Mean = 0.37 $\quad \sum(\%\ \text{deviation})^2 = 703$

Standard deviation $s = \sqrt{\frac{703}{7}} = 10\%$

Standard deviations for other elements computed similarly were

Nickel	8%	(5.73 ppm mean)
Tin	10%	(5.33 ppm mean)
Titanium	11%	(0.64 ppm mean)
Vanadium	6%	(1.49 ppm mean)
Cadmium	14%	(5.52 ppm mean)
Copper	21%	(0.14 ppm mean)
Cobalt	16%	(0.35 ppm mean)

Effect of Concentrate Matrix Composition

Working curves were compiled for Fe_2O_3 rich and Al_2O_3 rich base matrices and some variation was shown to exist in the intensity ratios of analysis pairs corresponding to the same trace element concentrations (see figs. 3a and 3b). For most elements the ratio of analysis line to that of the internal standard line is higher in the Al_2O_3 matrix, possibly because of the longer burn in this matrix. Mo is an exception, Mo 3170/Pd 3481 being higher in a Fe_2O_3 matrix. It is in any case desirable to prepare two sets of working curves corresponding to the two extremes of matrix composition and to use the appropriate set in any given case. Direct inspection of the spectrograms may be used to determine the iron or aluminium rich nature of the matrix. Scott (1945) and Ahrens (1950) have summarised the effects of matrix composition on spectral line intensity, giving several possible causes for such changes.

Use of Hydrochloric Acid for Initial Attack

Acetic acid was chosen rather than hydrochloric acid for the initial attack on the limestone to restrict as far as possible any attack on the clay minerals at this stage in the procedure. Some tests were made using 25% hydrochloric instead of acetic acid and table 3 shows the results obtained.

The fraction of the rock soluble in HCl was always greater than the acetic soluble fraction, particularly in impure limestones

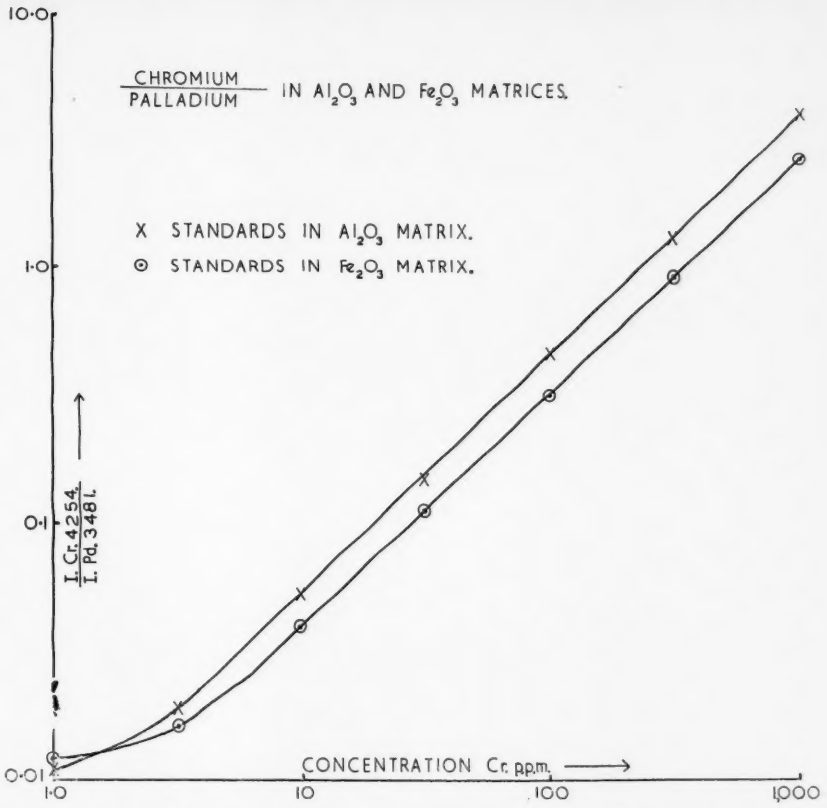

FIG. 3a.—The chromium working curve in Al_2O_3 and Fe_2O_3 matrices; illustrating the effect of matrix on the intensity ratio of analysis line to internal standard line. Chromium vs. palladium.

compared to those which are almost pure $CaCO_3$. Table 3 shows that the trace element contents in the hydrochloric soluble fraction are greater than in the acetic soluble fraction but the ratios for different elements in one rock are not constant as would be expected if the non-detrital fraction had been more completely removed by the stronger acid. Thus, provisionally, the higher contents in the hydrochloric soluble fraction are attributed to some attack on the detrital part of the rock. This interpretation is in harmony with the work of Ray, Gault, and Dodd (1957), who showed that hydrochloric acid of this strength attacks the lattice of the clay mineral hectorite and consequently may well attack other minerals of similar crystal structure.

SOME ILLUSTRATIVE RESULTS

A selection of results obtained during a geochemical study of limestones is presented in table 4. From the nature of the calculation described earlier the figures quoted for the acid soluble (non-detrital) fraction refer to the content of trace elements present in the total rock which is contained in this fraction. It is apparent from these results that the content of Ni, Co, Cr, and V in the acid soluble fraction is frequently so low that it would be below the detection limit if the evaporated soluble frac-

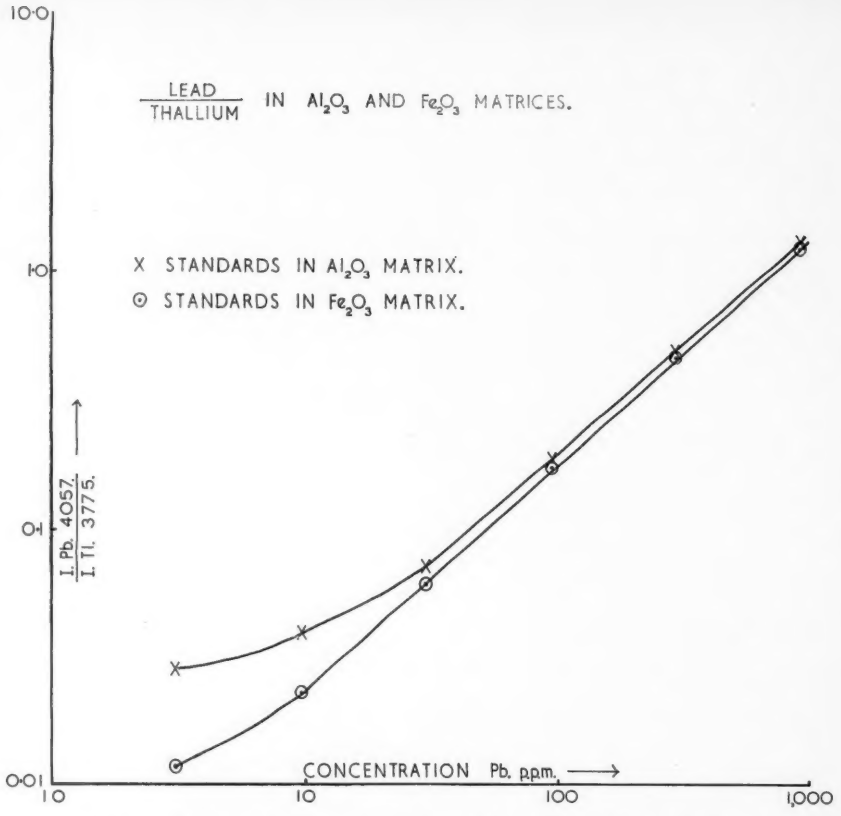

FIG. 3b.—The lead working curve in Al_2O_3 and Fe_2O_3 matrices; lead vs. thallium.

tion was arced directly. The application of the precipitation procedure puts values in the ashed concentrate well above detection limits and often on to the more reliable straight line portion of the working curves. The order of concentration from the acid soluble fractions is seventy times by the technique at present in use in this laboratory. It could be increased if less dilutent Al_2O_3 or Fe_2O_3 were used in the preparation of arcing mixtures and smaller electrodes adopted.

Determinations of total trace element contents of the rocks were made on samples heated to 900°C to drive off CO_2 and corrected for percentage loss in weight on heating. The results are also given in table 4. Standards used in this stage of the work were prepared in a base of heated $CaCO_3$ (CaO). Since the limestones are not pure $CaCO_3$ there may be a slight matrix effect error on these results but it should not be significant.

No determinations were made of the amounts of trace elements present in the residues from the acid attack (detrital fraction) but they can easily be obtained by direct subtraction of amounts present in the acid soluble fraction from those in the total rock. The values quoted in table 4 were obtained in this way.

Simple calculations give the actual contents of the different trace elements in the non-detrital and detrital fractions (as dis-

TABLE 3.—*Effect of using HCl instead of acetic acid as extractant*

Percentage increase in weight of ashed precipitate when HCl is the solvent

JE 6	41
DA 5	106
An 11	13.(5)

Percentage decrease in the weight of the insoluble residue when HCl is the solvent

JE 6	6
DA 5	14.(5)
AN 11	3

Trace element determinations using both acetic and hydrochloric acid as solvents, determinations in ppm

Limestone	Solvent	Ni	Co	Cr	V	Mo	Ag
JE 6	Acetic Acid	2.05	.183	.592	.633	< .014	*
	Hydrochloric Acid	2.18	.195	1.10	1.47	.054	.042
DA 5	Acetic Acid	1.03	.033	.718	2.8	< .049	*
	Hydrochloric Acid	2.92	.128	1.28	2.91	.042	.035
AN 11	Acetic Acid	7.91	1.39	1.24	3.07	<0.21	*
	Hydrochloric Acid	9.79	1.63	1.26	3.13	< .036	.13

* Below limit of detection.

tinct from their contributions to the total trace element contents of the rock). The results of such calculations are given in table 5. From them the ratios of contents of given trace elements in the non-detrital fraction to their contents in the detrital fraction may be determined. These ratios are truer representations of the detrital or non-detrital character of the elements than any that might be computed from the data in Table 4. We suggest they should be used to express the *sedimentary character* of an element in a given environment. For strict non-detrital elements values of these ratios should be >1 and for detritals <1. It is clear from table 5 that the four elements under discussion are essentially detrital in the sedimentary environments of the rocks studied, though exceptions do occur, for example, V in the Carboniferous cementstone from Linhouse Water, Scotland.

It is immediately apparent that all four elements occur in both the acid-soluble (non-detrital) and residual (detrital) fractions and are not found exclusively in one or the other. For Co and Cr the detrital contribution to the total trace element content is much greater than the non-detrital for most of these rocks; for Ni it is greater in five of the eight rocks studied, but not overwhelmingly so, and in the other three rocks the non-detrital contribution is greater than the detrital; for V the detrital contribution is greater in only three of the eight specimens, and only in one, the shaly Dockra Limestone from Ayrshire is it overwhelmingly so. The absolute amounts of such contributions will clearly depend on the proportions of the two fractions within any given specimen and might be expected to vary within a single bed or horizon. If, however, ratios of contributions of different elements are considered they should be independent of such variation. Table 4 also lists the ratios of Co contributions to those of Ni and Cr contributions to those of V. The Co/Ni ratio is greater in the detrital fraction in every case, as is the Cr/V ratio.

Ni shows a consistent tendency to enter the non-detrital fraction preferentially to Co so that the Co/Ni ratio in this fraction is consistently very low. In seven of the eight specimens examined the detrital fraction contains more Ni than Co, the usual relationship for total Ni and Co contents in shales (Rankama and Sahama, 1950; Mohr, 1955), but the Co/Ni ratio tends to be higher than in shales. It is apparent that

TABLE 4.—*Trace element data on some British limestones*

Rock	% insoluble in acetic acid	% soluble in acetic acid		Trace element contents in ppm				Trace element ratios	
				Ni	Co	Cr	V	Co/Ni	Cr/V
AN 13. Cambrian limestone, Durness, Scotland	5.91	94.09	Rock.	8.6	3.2	2.7	1.6	0.37	1.7
			Sol. fraction (non-detrital)	4.0	0.07	0.23	0.5	0.017	0.46
			Insol. fraction (detrital)	4.6	3.1 (3)	2.4 (7)	1.1	0.68	2.3
JE 6. Wenlock limestone (Silurian), Shropshire, England	3.39	96.61	Rock.	5.6	2.4	2.1	1.6	0.43	1.3
			Sol. fraction (non-detrital)	2.1	0.18	0.6	0.6	0.086	1.0
			Insol. fraction (detrital)	3.5	2.2 (2)	1.5	1.0	0.63	1.5
DA 5. Cornstone (Devonian), Balgraggen, Ayrshire, Scotland	1.69	98.31	Rock.	4.3	2.8	2.5	4.2	0.65	0.59
			Sol. fraction (non-detrital)	1.0	0.03	0.7	2.8	0.03	0.25
			Insol. fraction (detrital)	3.3	2.7 (7)	1.8	1.4	0.85	1.3
DA 12. Cementstone (Carboniferous), Linhouse Water, Scotland	45.08	54.92	Rock.	70	34	16	32	0.49	0.5
			Sol. fraction (non-detrital)	9.6	0.03	1.5	19	0.0031	0.079
			Insol. fraction (detrital)	60 (4)	33.9 (7)	14 (5)	13	0.57	1.1
DA 2/B. Dockra limestone (Carboniferous), Hassilhead, Ayrshire, Scotland	49.84	50.16	Rock.	83	26	26	13	0.31	2.0
			Sol. fraction (non-detrital)	26	6.0	1.7	1.2	0.23	1.4
			Insol. fraction (detrital)	57	20	24.3	11 (8)	0.35	2.1
AN 6. Bule Lias limestone (Jurassic), Lyme Regis, England	14.58	85.42	Rock.	23	6.0	8.8	15	0.26	0.59
			Sol. fraction (non-detrital)	12	0.8	3.3	9.7	0.067	0.34
			Insol. fraction (detrital)	11	5.2	5.5	5.3	0.47	1.0
AN 11. Upper White Oölite limestone (Jurassic), Osmington Mills, England	6.76	93.24	Rock.	13	3.3	4.2	5.1	0.25	0.82
			Sol. fraction (non-detrital)	7.9	1.4	1.2	3.1	0.18	0.39
			Insol. fraction (detrital)	5.1	1.9	3.0	2.0	0.37	1.5
AN 9. Upper Portland Freestone (Jurassic) Portland Bill, Dorset, England	2.13	97.87	Rock.	6.0	2.0	0.88	2.3	0.33	0.38
			Sol. fraction (non-detrital)	5.7	0.35	0.37	1.5	0.061	0.25
			Insol. fraction (detrital)	0.3	1.6 (5)	0.51	0.8	5.5	0.64

TABLE 5.—*Trace element contents of detrital and non-detrital fractions of rocks in table 4 in ppm*

Rock. Nos. as in Table IV	Ni			Co			Cr			V		
	Soluble fraction (Non-detrital)	Insoluble fraction (detrital)	Non-detrital / detrital	Soluble fraction (non-detrital)	Insoluble fraction (detrital)	Non-detrital / detrital	Soluble fraction (Non-detrital)	Insoluble fraction (detrital)	Non-detrital / detrital	Soluble fraction (Non-detrital)	Insoluble fraction (detrital)	Non-detrital / detrital
AN 13	4.2	79	0.053	0.07	53	0.0013	0.25	42	0.0060	0.56	17	0.033
JE 6	2.1	100	0.021	0.19	66	0.0029	0.61	44	0.014	0.66	28	0.024
DA 5	1.0 (5)	190	0.0055	0.03	160	0.00019	0.73	100	0.0073	2.9	85	0.034
DA 12	17	130	0.13	0.05	75	0.00067	2.8	32	0.087 (5)	35	28	1.2 (5)
DA 2/B	53	110	0.48	13	40	0.32 (5)	3.3	50	0.066	2.5	25	0.10
AN 6	14	77	0.18	0.92	36	0.026	3.9	37	0.11	11	37	0.30
AN 11	8.5	82	0.10	1.5	28	0.054	1.3	43	0.030	3.3	30	0.11
AN 9	5.9	15	0.39	0.36	76	0.0047	0.38	24	0.016	1.5	37	0.041

during the processes of weathering, erosion, transportation, and deposition Ni and Co differ slightly in their behaviour and some separation of the two becomes effective. Before such differences in behaviour can be fully understood more data must be accumulated on their effects, and at present the technique described here appears a promising method for accumulating such data.

The Cr/V ratio in the non-detrital fraction is less consistent than Co/Ni though there is a tendency for V to enter this fraction preferentially to Cr in these specimens. The detrital fraction contains at least as much Cr as V in seven of the eight rocks. The Cr/V ratios in these fractions of the different specimens are surprisingly constant in view of the differences of age and depositional environment represented by these rocks. It is not intended in this paper to explore reasons for such features, but merely to draw attention to the type of information disclosed by the use of the technique described here.

Of course, this does not imply that they would be necessarily detrital in other sedimentary environments and further studies on other types of sediment from different environments are now being made to ascertain the character of these elements under other conditions. In the limestones studied here the sedimentary characters of the elements vary and Co and Cr are more strictly detrital than Ni and V. There is some suggestion in table 5 that the sedimentary character of Ni and Co was slightly different during the formation of the Mesozoic rocks from what it was during the formation of the Lower Palaeozoic. If this should be substantiated by the accumulation of further data it will raise interesting questions concerning the nature of weathering, transportation and deposition in the past.

This paper is concerned principally with a technique of geochemical investigations and the illustrative results presented are too few to permit any conclusions to be drawn. They are introduced here to show how the data can be used to display the behaviour of the chemical elements in the sedimentary environment more clearly than do the determinations of total trace element contents of the rock. Our full results will be published in later papers.

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REFERENCES

AHRENS, L. H., 1950, Spectrochemical analysis. Addison-Wesley Press, Cambridge, Mass., 267 p.

FLAGG, J. F., 1948, Organic reagents used in gravimetric and volumetric analysis, Chemical Analysis IV. Interscience, New York. 300 p.

HEGGEN, G. E. AND STROCK, L. W., 1953, Determinations of trace elements combining chemical enrichment and spectro-chemical methods: Anal. Chem., v. 25, p. 859–863.

KRYNINE, P. D., 1948, The megascopic study and field classification of sedimentary rocks: Jour. Geology, v. 56, p. 130–165.

MITCHELL, R. L., AND SCOTT, R. O., 1947, Concentration methods in spectrochemical analysis. II. Recovery of trace constituents in plant materials and soil extracts by mixed organic reagents: Soc. Chem. Industry Jour. (Trans.), v. 66, p. 330–336.

———, 1948, Applications of chemical concentration by organic reagents to spectrographic analysis: Spectrochimica Acta, Bd. 3, p. 367–378.

MOHR, P. A., 1955, A geochemical study of the Lower Cambrian Manganese Shale group sediments of the Harlech Dome. Unpub. Ph.D. thesis, University of Manchester.

NOCKOLDS, S. R. AND MITCHELL, R. L., 1948, The geochemistry of some Caledonian plutonic rocks: a study in the relationship between the major and trace elements of igneous rocks and their minerals: Royal Soc. Edinburgh Trans., v. 61, p. 533–575.

NOCKOLDS, S. R. AND ALLEN, R., 1953, The geochemistry of some igneous rock series: Geochimica et Cosmochimica Acta, v. 4, p. 105–142.

———, ———, 1954, The geochemistry of some igneous rock series: Part II: Geochimica et Cosmochimica Acta, v. 5, p. 245–285.

———, ———, 1956, The geochemistry of some igneous rock series III: Geochimica et Cosmochimica Acta, v. 9, p. 34–77.

RANKAMA, K. AND SAHAMA, T. G., 1950, Geochemistry. University of Chicago Press. 912 p.

RAY, S., GAULT, H. R. AND DODD, C. G., 1957, The separation of clay minerals from carbonate rocks: Am. Mineralogist, v. 42, p. 681–686.

RUSHTON, B. J. AND NICHOLLS, G. D., 1957, A spectrographic scheme for the determination of Al, Ti, Fe, Ca, Mg and Mn in silicates: Spectrochimica Acta, v. 9, p. 287–296.

SCOTT, R. O., 1945, The effect of extraneous elements on spectral line intensity in the cathode-layer arc: Soc. Chem. Industry Jour. (Trans.), v. 64, p. 189–194.

SCOTT, R. O. AND MITCHELL, R. L., 1943, Concentration methods in spectrographic analysis. I. Recovery of cobalt, nickel, molybdenum, copper and zinc from plant materials and soil extracts by 8-hydroxyquinoline: Soc. Chem. Industry Jour. (Trans.), v. 62, p. 4–8.

SHAW, D. M., 1952a, The geochemistry of thallium: Geochimica et Cosmochimica Acta, v. 2, p. 118–154.

———, 1952b, The geochemistry of indium: Geochimica et Cosmochimica Acta, v. 2, p. 185–206.

WAGER, L. R., AND MITCHELL, R. L., 1943, Preliminary observations on the distribution of trace elements in the rocks of the Skaergaard intrusion, Greenland: Mineralog. Mag. v. XXVI, p. 283–296.

———, 1951, The distribution of trace elements during strong fractionation of basic magma—a further study of the Skaergaard intrusion, East Greenland: Geochimica et Cosmochimica Acta, v. 1, p. 129–208.

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FIGS. 1–2, DECEMBER, 1958

"SIZE FACTORS," A MEANS OF ANALYSIS OF DATA FROM TEXTURAL STUDIES OF TILL[1]

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ABSTRACT

Tills on the Allegheny Plateau in northeastern Ohio and northwestern Pennsylvania can be differentiated on the basis of percentages of sand, silt, and clay. However, for comparing size analyses of tills from very large populations it is convenient to reduce each analysis to a single number. The median size is the most useful single number; however, it can be determined only from a detailed analysis, which is very time consuming. Plotting the percentage of sand and clay on a rectangular graph and dividing the area into numbered narrow "zones" provides a series of numbers called "size factors" which serve the same purpose as median diameters. An approximation to median size is obtained by reference to a chart.

INTRODUCTION

This paper is concerned with a method of graphical representation and analysis of data obtained from the mechanical analysis of till. The method is one of those to be used by our group in reporting work, now approaching completion, on the textures of the tills of northeastern Ohio and northwestern Pennsylvania.

A study of the composition and texture of more than 1000 till samples from the Allegheny Plateau in northeastern Ohio and northwestern Pennsylvania by means of grain size analysis (White and Shepps, 1952; Shepps, 1953), heavy minerals, clay mineralogy (Droste, 1956a; 1956b; Droste and Tharin, 1958), pebble counts, microfabrics (Sitler and Chapman, 1955), and carbonate content has been undertaken at the University of Illinois by Professor G. W. White and his associates with the support of a National Science Foundation grant. The cooperation of Professor White and Mr. James C. Tharin in this study is appreciated.

THE PROBLEM

The grain size analysis of a till sample is commonly illustrated as a histogram or cumulative curve. In order to analyze the data more readily the data are reduced to statistical values such as the arithmetic mean, median, coefficient of sorting, and standard deviation; or they may be given as sand/clay or other ratios. In an earlier paper (Shepps, 1953) information on till texture in a part of northeastern Ohio when presented as percentages of sand, silt, and clay plotted on triangular diagrams clearly showed comparisons and relationships of several till sheets. The triangular diagram was successfully used to represent 76 samples, but the triangular diagram became cumbersome when a group of several hundred samples was studied.

For drawing isopleths and for other regional studies a means was sought by which the results of each analysis could be reduced to a single number that would represent an accurate statement of the texture of the sample. Any single number cannot include all of the information in a till analysis, but a single number can be selected which, when compared with numbers derived from other analyses, will enable one to (1) study the distribution of texture within a single till sheet, to (2) compare till sheets, and to (3) determine the reliability of texture as a tool for correlation.

SIZE FACTORS

All of the available single numbers, such as median and mean, were tested to determine if they would be acceptable as the single number sought. All values except the arithmetic mean and the median were discarded. The arithmetic mean and median most nearly characterize the texture of a till sample, but mean and median values can only be obtained from a detailed mechanical analysis of each till sample. The difficulties

[1] Manuscript received May 15, 1958.

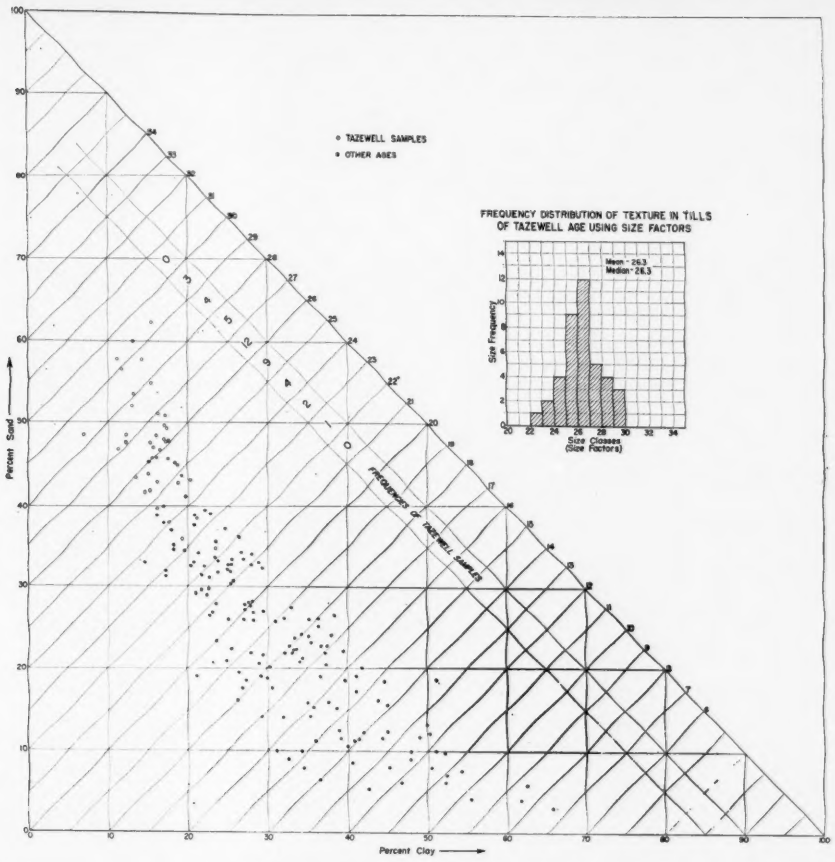

FIG. 1.—Graph showing size factors.

inherent in undertaking 1000 complete mechanical analyses are great.

In one part of the study the percentages of sand, silt, and clay in 199 samples of calcareous till were determined. Complete pipette analyses were run for the first fifty samples. It was found, however, that the percentages of sand, silt, and clay were sufficient to characterize the texture of a till and that more complete analyses were not necessary (Shepps and White, 1952; Shepps, 1953). The remaining samples were then analyzed for sand, silt, and clay content alone. The triangular diagram presents sand, silt and clay percentages as three variables. It is readily possible to reduce the number of variables to two by plotting the data on a rectangular diagram (figure 1) showing sand and clay. The percentage of silt is equal to the sum of the percentage of sand and clay subtracted from 100. Sand and clay were chosen because they show the greatest variation. Sand is plotted on the abscissa and clay on the ordinate.

The scatter of points on the graph forms a band trending from about 60 percent clay on the abscissa to 70 percent sand on the ordinate. The samples plotted have been taken from till sheets determined from stratigraphic and regional tracing to be of

four different ages (White, 1953, 1957; White, Droste, Sitler and Shepps, 1957). By plotting the samples using a different symbol for each age (only one age, Tazewell, is differentiated in figure 1), it has been found that variation across the band is a variation *within* the separate till sheets only. Variation along the band is variation *between as well as within* till sheets. The statistical sorting value for each sample was plotted at the point on the graph for each sample and these values contoured. It was found that "lines of equal sorting" are parallel to the band. This means that variation within till sheets "across" the band is due to sorting. In the same manner, median values when contoured indicate that "lines of equal median size" are approximately perpendicular to the band. In this case, variation between till sheets, and to some extent variation within till sheets, is reflected in variation in median size. "Lines of equal mean size" are similarly perpendicular to the band, but show more "wandering" than the median lines. The greater "wandering" of the lines of equal mean size reflects the fact that the arithmetic mean is influenced more than the median by extreme values.

Because variation across the band is due to variation in sorting and because sorting is similar with each till sheet, sorting is not a factor which distinguishes between till sheets and was consequently discarded because one of the major objectives of this study is to analyze the variation between till sheets. The effect of discarding this factor is to narrow the band to a line. The texture of any sample can be given by stating the position of that sample on the line. This postion can be given by dividing the line into a series of numbered classes. The same results can be obtained without physically projecting the points to a line by drawing a series of lines across the graph perpendicular to the band. The space between any two of the lines represents a size class. In figure 1 these lines are drawn with a class interval chosen to fit the diagram and large enough to include a reasonable number of samples. The line passing through the origin is arbitrarily assigned the value of 20. The other lines are assigned consecutive numbers increasing toward 100 percent sand and decreasing in the opposite direction. The arbitrary numbers will be called "size factors." A sample has a size factor of 9, for example, if the dot for that sample on the graph (fig. 1) falls on line number 9 or anywhere betweeen line number 9 and line number 10. Or in a specific case, a sample falling between line 9 and line 10 can be interpolated as having a value between 9 and 10, for example, 9.3.

It is apparent in figure 1 that the larger the size factor the coarser the texture; conversely, the smaller the size factor the finer the texture. It is assumed that a size factor adequately represents the texture of an individual sample and thereby constitutes the single number which has been sought. Size factors can be used to plot a curve of textural distribution for the tills of each till sheet. Using statistical values derived from such curves it is possible to compare till sheets and to test the validity of texture as a tool for correlation. Using size factors it is possible to plot individual samples on a map and draw isopleths in order to study the variation of texture with geography.

Size factors have the linear relationship to median size shown in figure 2, which is based upon the previously published complete analyses of 50 samples (Shepps, 1953, table 2, p. 37).[2] The 50 samples and the 199 samples in this study were picked at random from the same till sheets; consequently figure 2 can be used with the samples presented here or with any other group of samples from these same till sheets. It is assumed that the linear relationship based upon 50 samples would change very little if it were based on a larger number of samples or on different samples from the same tills. Median size measurements which have been made in terms of size factors can be converted by means of the regression line in figure 2 to "approximate" median size in millimeters.

USE OF SIZE FACTORS

In figure 1 the samples determined in the field as Tazewell are shown as circles and all other samples as dots. By summing the frequency of Tazewell samples in each of the size classes, a histogram of sample frequency vs. texture (in terms of size factors) was constructed as shown in the upper right of figure

[2] In Shepps, 1953, the heading in table 2 erroneously labeled "mean" should read "median."

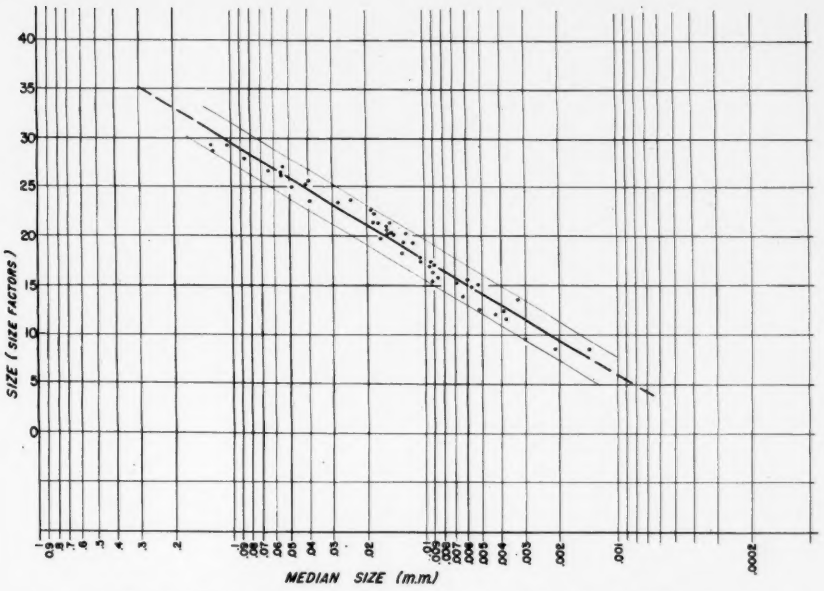

FIG. 2.—Graph showing relationship between size factors and median size.

1. This histogram shows that the samples from the Tazewell till sheet are approximately normally distributed. The arithmetic mean of this distribution is 26.3 size factors, the median is also 26.3 factors, and the standard deviation is 1.15 in terms of size factors. The Tazewell till can be seen to have an approximate median size of .05 mm, by reference to figure 2. Similar values can be determined for each of the other till sheets. Having such values it is possible to perform an analysis of variance on the data in order to measure and discuss the variation within and between till sheets and to test the value of texture as a tool for correlation.

REFERENCES

DROSTE, J. B., 1956a, Clay minerals in calcareous till in northeastern Ohio: Jour. Geology, vol. 64, p. 187–190.

———, 1956b, Alteration of clay minerals by weathering in Wisconsin tills; Geol. Soc. America Bull., v. 67, p. 911–918.

———, AND THARIN, J. C., 1958, Alteration of clay minerals in Illinoian till by weathering: Geol. Soc. America Bull., v. 69, p. 61–68.

SHEPPS, V. C., 1953, Correlation of the tills of northeastern Ohio by size analysis: Jour. Sedimentary Petrology, v. 23, pp. 34–48.

SITLER, R. F., AND CHAPMAN, C. A., 1955, Microfabrics of till from Ohio and Pennsylvania: Jour. Sedimentary Petrology, v. 25, p. 262–269.

WHITE, G. W., 1953, Geology and water-bearing characteristics of the unconsolidated deposits of Cuyahoga County: The ground-water resources of Cuyahoga County, Ohio, Ohio Division of Water, Bull. 26, p. 36–42.

———, 1957, Wisconsin glacial deposits of northeastern Ohio (Abstract): Geol. Soc. America Bull., v. 68, p. 1902.

———, DROSTE, J. B., SITLER, R. F., AND SHEPPS, V. C., 1957, Glacial deposits of northwestern Pennsylvania (Abstract): Geol. Soc. America Bull., v. 68, p. 1902–1903.

———, AND SHEPPS, V. C., 1952, Characteristics of Wisconsin tills in northeastern Ohio (Abstract): Geol. Soc. America Bull., v. 63, p. 1388.

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CORROSION ZONES: A MODIFIED HYPOTHESIS OF THEIR ORIGIN[1]

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ABSTRACT

New evidence suggests that the formation of corrosion zones takes place by solution in the intertidal zone, and that they are genetically related to similar surfaces that have undergone abrasion. Abraded and corroded diastemic surfaces are viewed as the end-members of a continuous, intergrading series.

INTRODUCTION

Highly irregular and dove-tailed diastemic bedding surfaces in limestone have been called corrosion surfaces (Weiss, 1954) because of their apparent origin by etching of the subjacent bed before the deposition of the superjacent bed. Such surfaces occur within a certain interval of rock; this interval, together with mineral and textural abnormalities related to the corroded surface, constitutes the corrosion zone.

Two recent papers (Revelle and Emery, 1957; Dott, 1958), which contain descriptions of limestone surfaces similar to corrosion zones, give a clearer understanding of the origin of these zones. Certain other irregular diastemic surfaces, which are considered briefly below, help us distinguish those kinds that are genetically related to ideal corrosion zones from those that are only superficially similar.

Different hypotheses of the development of corrosion zones have been stated by Weiss (1957, p. 1052) and Prokopovich (1955). Although Prokopovich (1955, p. 207, 211, 213) uses a broader definition of what constitutes a corrosion zone, and places more emphasis on the mechanical aspects of their formation, the hypotheses are similar. Separately or together, they are reasonable explanations of the origin of these peculiar sedimentary features, even though it has been necessary to invoke special conditions to explain the dissolution of limestone by sea water. Weiss, especially, has assumed the inability of normal sea water to accomplish such dissolution, especially of the dense varieties of limestone such as are found in the Middle Ordovician of Minnesota. That masses of reef limestone might be planed off by solvent action, perhaps because of special effects at the water's edge, did not seem to be applicable to the etching of broad corrosion-zone surfaces.

[1] Manuscript received May 26, 1958.

CORROSION SURFACES AND ZONES NEWLY RECOGNIZED

Revelle and Emery (1957) show that normal sea water can indeed dissolve limestone in the intertidal zone, and how the process operates. In so doing they not only resolve the long-standing apparent conflict between geological and chemical evidence concerning such solvent action, but they also illustrate limestone surfaces that certainly are corrosion zones in process of development. Etched surfaces of limestone on Bikini and Rongerik (Revelle and Emery, 1957, pl. 225) are like the typical dove-tailed corrosion surfaces described by Weiss (1954). To the writer's knowledge, these are the first modern surfaces of this type to be reported from a marine environment, although similar surfaces of freshwater origin were illustrated by Hudson (1910, pl. 17).

The similarity of figure 4 of Weiss (1954) and figure B, plate 225 of Revelle and Emery (1957) is unmistakable. Likewise, the hackly profiles of the Ordovician surfaces illustrated by Weiss compare closely with the textures of the surfaces shown in figures A and C of the same plate by Revelle and Emery. The sand that partly fills the pits shown in their figure B is analogous to the carbonate-cemented sand and sandy carbonatite that lies over the lowest of the three corrosion surfaces at the top of the Pecatonica Member of the Platteville Formation (Weiss, 1954, figs. 1, 2, 3).

An excellent example of a corrosion zone in the middle Sequanian (Upper Jurassic) near Bourges, France has been described by

Ellenberger (1947, p. 271). A deeply corroded and perforated bed of lithographic limestone is overlain by detrital limestone containing broken and worn shell fragments. The corroded surface is complexly irregular, with a relief of 10–20 cm, and the adjacent beds are intimately interlocked. In addition, the subjacent bed is irregularly perforated by tortuous ragged tubules to a depth of more than 70 cm, and the overlying rock fills these cavities. Ellenberger does not suggest an origin for the tubules, and his illustration (fig. 9) gives no distinct clues, but there is little doubt that the dove-tailed contact of the two beds is a characteristic corrosion zone.

ABRADED SURFACES

Dott has described some scoured diastems that occur in Pennsylvanian limestones of eastern Nevada (Dott, 1958, p. 5; pl. 1, fig. 1). Although they resemble superficially the corrosion zones in Minnesota, no real interlocking or dove-tailing of the adjacent strata seems to exist. He reports (personal communication) that the diastems considered in his paper have a limited lateral extent, probably no more than a few tens of feet, and that they show no concentration of pyrite, limonite, or carbonaceous material along or above the pitted surface. These Pennsylvanian diastems are overlain by very sandy limestone, however. Dott concluded that these surfaces are the result of mechanical erosion. Clearly, they are not the same as the corrosion zones of the Ordovician of Minnesota, but the elements of similarity suggest that the two kinds of features are related.

An apparently similar kind of surface in the Lower Cretaceous rocks of the Salève Range near Geneva, Switzerland, has been described by Carozzi (1953). The diastemic surface is known at only one locality, and is only about 60 cm wide, although it has a relief of 50 cm. The diastem occurs between the shelly oölitic Upper Hauterivian limestone and the poorly bedded marly Lower Barremian limestone. This contact has heretofore always been considered transitional, but it apparently is not often favorably exposed. The occurrence described by Carozzi is not dove-tailed, but abundant quartz sand, cemented poorly by calcite, lies in the channel in the diastemic surface. He believes the quartz sand to be of eolian origin, and because some of the quartz grains are larger than any in nearby older rocks, that they come from a distant source. He concludes that the diastem gives evidence of emergence followed by subaerial erosion. The importance of this diastem is that it shows some similarity to the corrosion zones described earlier by the present writer, whatever its regional significance.

HYPOTHESIS OF INTERTIDAL CORROSION

A revised working hypothesis for the origin of the interlocking surfaces of the Ordovician corrosion zones is suggested by the evidence of Revelle and Emery and of abraded diastemic surfaces in limestones: that corrosion surfaces are developed by the solvent action of sea water in the intertidal zone, and that they may grade laterally, through corroded and abraded surfaces, to abraded surfaces.

The similarity of corrosion surfaces to modern surfaces etched by the sea, the freedom from the need to postulate special local stagnant acid conditions of the sea bottom, and the freedom from dependence on concentrations of H_2S for a solvent, all recommend the intertidal hypothesis.

In apparent opposition to the hypothesis of intertidal corrosion is the fact that significant amounts of pyrite and collophane lie on some of the Ordovician corroded surfaces. These substances can hardly be thought of as having been formed in the well-aerated intertidal zone. However, the pyrite may be of diagenetic origin, and the polished granules and pebbles of collophane may have been introduced. The soft reddish flakes of collophane (Weiss, 1957, p. 1031) are not readily accounted for, but may be an autochthonous organic residue.

For characteristic corrosion surfaces to have been etched in the zone of wave action means that the sediment of the bottom must have been moderately well cemented before the etching process started. Over large areas the Ordovician corrosion zones have fairly smooth corroded surfaces, rather than the more or less dove-tailed surfaces that are considered typical. This fact suggests that dove-tailing may have developed either where the subjacent rock was indurated or where wave action was minimal, and that

the smoother parts of the surface were more abraded than corroded. This view is in accord with that of Prokopovich (1955), who noted some evidence of mechanical effects in the formation of the corrosion zones of Minnesota. The occurrences reported by Carozzi (1953) and Dott (1958) give additional weight to the view that chemically corroded surfaces are the end members of a series which ranges through surfaces of mixed origin to those that are more abraded than corroded. The relative importance of corrosion and abrasion of limestones can vary from place to place or from time to time, according to special circumstances of the erosional environment. This may be true although the general condition necessary for the formation of broad marine diastemic surfaces on limestones remains the same: that is, exposure of a bedding surface in the intertidal zone.

The gradation from etched hackly surfaces near the high tide mark to smooth abraded surfaces near the low tide level, in reef limestones off the coast of western Australia, recorded by Fairbridge (1948, p. 26), is instructive. His description suggests that corrosion surfaces are forming there, although one cannot demonstrate a correspondence between those surfaces and those of the Ordovician of Minnesota from his text and illustrations.

The hypothesis of intertidal corrosion holds certain implications with respect to tectonic conditions and rates of lithification. The sea bottom must either have been raised into the intertidal zone and subsequently lowered again, or there must have been eustatic changes of sea level. The near parallelism between successive corrosion zones, bedding planes, and lithologic boundaries (Weiss, 1957, pl. 5) shows that no structural derangement accompanied these changes. The period of exposure of the bottom in the intertidal zone must have been very short (Weiss, 1957, p. 1052).

SURFACES OF OTHER ORIGINS

Wells (1944, p. 294) has described local occurrences wherein the bone beds of the Devonian limestones of central Ohio lie on mudcracked surfaces or on scoured surfaces. He believes that the mudcracked surfaces and the deposits lying directly on them underwent eolian action. The scoured surfaces are attributed to submarine scour above wave base, which may have occurred in an intertidal zone, of course. Nevertheless, these surfaces are nowhere corroded, nor do they suggest corrosion zones by their appearance. The mudcracked surfaces are not in any way related to corrosion zones, and the scoured surfaces seem to be instances of local submarine scour that are not really comparable to intertidal flats in reef limestone (Fairbridge, 1948, p. 26) or to the abraded surfaces in the Ordovician of Minnesota.

SUMMARY

Although the data now recorded concerning corrosion zones do not indicate their origin with certainty, the fact that similar surfaces can be seen in the process of formation today strongly suggests that they originated in the intertidal zone. An extension of this hypothesis relates the purely corroded surfaces to those that have been partly or largely abraded, but makes the term "corrosion zone" somewhat inappropriate for certain of these features. Inconsistencies of nomenclature will not arise if the term is restricted to those diastemic surfaces that shown some definite evidence of chemical formation. The process of intertidal corrosion should be held as a working hypothesis in any further investigations of these peculiar features.

REFERENCES

CAROZZI, A., 1953, Une épisode continental à la limite hauterivien-barrémian au Grand-Salève: Archives des Sciences, v. 6, fasc. 6, p. 393–396.

DOTT, R. H., JR., 1958, Cyclic patterns in mechanically deposited Pennsylvanian limestones of northeastern Nevada: Jour. Sedimentary Petrology, v. 28, p. 3–14.

ELLENBERGER, F., 1947, Le problème lithologique de la craie durcie de Meudon, Banc-limites et "contacts par racines": lacune sous-marine ou émersion?: Soc. Géol. France Bull., 5th sér., v. 17, p. 255–274.

FAIRBRIDGE, R. W., 1948, Notes on the geomorphology of the Pelsart group of the Houtman's Abrolhos Islands: Jour. Royal Soc. Western Australia, v. 33, p. 1–43.

HUDSON, G. H., 1910, Joint caves of Valcour Island—Their age and their origin: New York State Mus. Bull. 140, p. 161–196.

PROKOPOVICH, N., 1955, The nature of corrosion zones in the Middle Ordovician of Minnesota: Jour. Sedimentary Petrology, v. 25, p. 207–215.

REVELLE, R. AND EMERY, K. O., 1957, Chemical erosion of beach rock and exposed reef rock: U. S. Geol. Survey Prof. Paper 260-T, p. 699–709.

WEISS, M. P., 1954, Corrosion zones in carbonate rocks: Ohio Jour. Sci., v. 54, p. 289–293.

———, 1957, Upper Middle Ordovician stratigraphy of Fillmore County, Minnesota: Geol. Soc. America Bull., v. 68, p. 1027–1062.

WELLS, J. W., 1944, Middle Devonian bone beds of Ohio: Geol. Soc. America Bull., v. 55, p. 273–302.

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FIGS. 1–3, DECEMBER, 1958

NOTES ON DIAGENETIC DOLOMITIZATION[1]

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ABSTRACT

Replacement of carbonate ooze containing metastable aragonite and magnesian calcite by magnesium-bearing solutions during diagenesis possibly occurs in various environments and under varying chemical conditions, but it is believed that secondary porosity developed in the calcite-dolomite replacement provides some of the avenues for ionic diffusion and for the escape of carbon dioxide. The intergranular film could play an important role in effecting transfer of magnesium ions in, and calcium ions out, through the unstable crystalline water meshwork in this film during late diagenesis.

INTRODUCTION

Diagenesis of carbonate ooze leading to formation of dolomite involves a series of processes possibly operating today under conditions of temperature and pressure normal to the earth's surface. These processes very likely include biologic, physical, and chemical effects concomitant with sedimentation and during the interval leading to induration of the sediment (fig. 1). According to Strakhov (1953, p. 19), the present day formation of dolomite in Lake Balkhash has been definitely established. Geologists have conflicting theories concerning secondary dolomitization, whether the processes operated only in the past or still operate today. This paper advances a few ideas—not necessarily new—which bear on the problem.

REALMS OF DIAGENETIC DOLOMITES

The temptation is strong among geologists to subscribe, wholly or in part, to the statement that "the present is the key to the past" when trying to visualize environments of carbonate deposition. While it is true that one should not disregard the spirit of uniformitarianism, caution should be exercised before insisting that only the processes which operate today should be used to assess conditions in the geologic past. Clues are gathered from the study of recent marine sediments, and these can be judiciously utilized in the light of available scientific knowledge.

Calcium carbonate can accumulate as a chemical precipitate, as a clastic aggregate ("glomeroclasts"), and in numerous other forms. Whatever its form, either as a lime mud (comparable to drewite) consisting of aragonite needles, or as a reef, biostrome, fossiliferous-fragmental ("hash") bed, a calcarenite, or various associations, $CaCO_3$ is capable of being replaced. Diagenetic dolomitization is particularly effective when the calcium carbonate is metastable and is in a realm conducive to replacement. The environmental conditions leading to direct precipitation of dolomite from sea water have been discussed by Chilingar (1956a).

Sites of maximum carbonate sedimentation today are found in the neritic zone on banks and platforms, particularly where biologic and physicochemical conditions provide optima. Atolls, such as Funafuti, and carbonate platforms such as the Bahama and Florida types, are also realms in which diagenetic dolomitization possibly may occur. Mention should also be made of the tidal-flat as a site of initial diagenetic transformation of carbonate ooze. Similar if not identical environments may well have characterized the geologic past, locally at least. Studies conducted on the Bahama Bank (Newell and Rigby, 1957) suggest various possible environments for carbonate deposition; these may also become sites of subsequent dolomitization. Teodorovich (1955, p. 77) believes that slow, warm bottom currents often play an important role in the formation of marine replacement dolomites. Furthermore, Fairbridge (1957) has outlined many of the problems connected with dolomite formation, particularly the modern environments of marine magnesium enrichment.

[1] Manuscript received March 27, 1958.

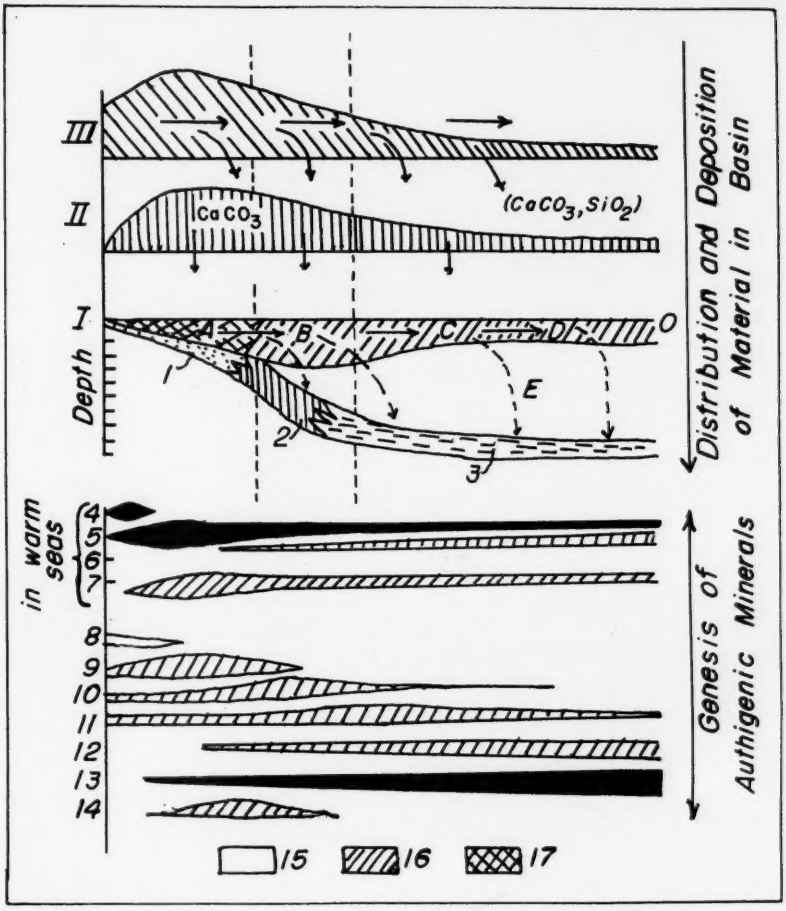

FIG. 1.—Zonation of new mineral formations in recent seas and in Cenozoic and Mesozoic Basins (after Strakhov, 1953, p. 26).

I—Progress of mechanical deposition of clastic material;
II—Progress of biologic deposition of components;
III—Progress of chemical precipitation of components;
A—turbid zone of fine-grained material, and its carrying out from near-shore zone into more central parts of the basin; B—areas of currents usually of circulatory type; C–D—surface zone of agitation and wind currents in central parts of basins; E—deep, quiet (with very slight movements of water) horizons of pelagic part of basins. Arrows show carrying out of fine material from the zone of turbidity to the more central parts of the basin; dashed arrows—hypothetical trajectories of particles falling to the bottom.
1—sands; 2—siltstones; 3—pelites; 4—$CaCO_3$, oölites;
5—biogenous and chemically precipitated $CaCO_3$; 6—diagenetic $CaCO_3$ (bacterial); 7—various forms of diagenetic dolomite; 8—Fe_2O_3, oxides of Mn, Al_2O_3; 9—leptochlorites;
10—glauconite; 11—carbonates of Fe and Mn (in muds without $CaCO_3$ or having very small $CaCO_3$ content); 12—sulfides of Fe, Mn (Cu, etc.) in muds with high $CaCO_3$ content;
13—biogenically formed SiO_2; 14—primary and diagenetic phosphorites; 15—minerals forming through direct precipitation from water; 16—diagenetic minerals;
17—partly primary, partly diagenetic minerals.

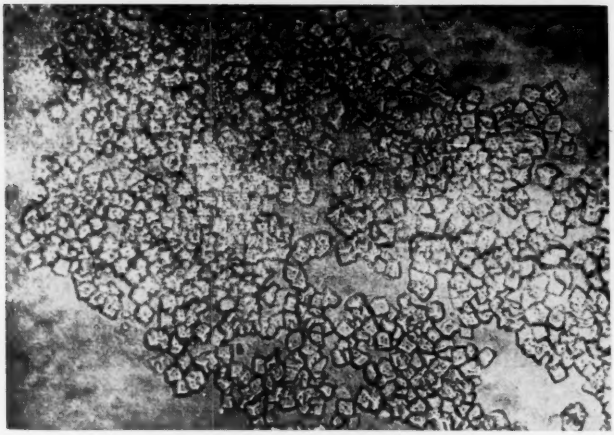

FIG. 2.—Dolomite rhombohedra. ×240. One nicol. Index of refraction 1.677. (After Kazakov, Tikhomirova and Plotnikova, 1957, p. 48.)

CHEMISTRY OF DIAGENESIS

Diagenetic dolomites have formed in the past. Numerous mottled dolomites are reported in the literature as cases of "arrested diagenesis." The geologist enters the realm of hypothesis, however, in asserting that dolomitization is going on under submarine conditions at the present time. At first sight this seems paradoxical. It is known, for example, that Mg^{++} ions are available in solution, and they occur under certain conditions in the crystal structure of calcite in warm sea water. In this metastable condition the carbonate is available for diagenetic changes. Also, aragonite is metastable and therefore can change to dolomite providing the Mg^{++} ions are available during diagenesis. It seems that the primary carbonate should be in an environment of sufficient alkalinity ($\Sigma\ HCO_3^- + CO_3^=$) to effect dolomitization; in addition certain catalysts may be required, possibly along with somewhat elevated temperature and pressure (yet still in the sedimentary realm). Kazakov, Tikhomirova, and Plotnikova (1957, pp. 47–50) obtained dolomite rhombohedrons (fig. 2) at 150° C after 90 hours from the following initial solution (closed system): CaO—52 mg/l, MgO—622 mg/l, CO_2—1358 mg/l, alkalinity—30.5 mg-equ/l, and pH—7.94. The chemistry of the final equilibrium solution was as follows: CaO—28 mg/l, MgO—86 mg/l, CO_2—412 mg/l, alkalinity—6.1 mg-equ/l, and pH—6.66. High alkalinity and low pH also prevailed during the precipitation of dolomite out of sea water at moderate CO_2 pressure (Chilingar, 1956b, p. 2261). As to whether high alkalinity and low pH are also necessary for the secondary diagenetic dolomitization or not has not been definitely established to date. Some dolomite forms in Lake Balkhash where the pH of the water is equal to 8.1–9.4 (Strakhov, 1953, p. 19).

Geochemical data indicate that at present the concentrations of Mg^{++} and Ca^{++} in the ocean are 1297 and 408 ppm, respectively. Geologists, however, cannot be sure that this Mg:Ca ratio of about 3:1 was obtained during any or of all, say, the Paleozoic (Chilingar, 1956b, p. 2263). Influx of Mg^{++} ions into carbonate muds may occur as a result of reduction of the sulfate ion if Mg^{++} is combined with $SO_4^=$ in sea water.

According to Strakhov (1956a, p. 19), if sulfate present in the mud, having a moisture content of 75 percent, undergoes complete reduction, it will give rise to 0.26 percent sulfur which can form pyrite with available iron. Thus, the amount of pyrite in dry sediment should be present in an amount of about 0.5 percent. Normal content of pyrite in clayey marine sediments ranges from a

small fraction of one percent to one percent (rarely higher). Thus the sulfate ions used in the formation of pyrite probably come mostly from the initial (connate) water trapped in the sediment, and there seems to be no appreciable diffusion of sulfate ions from the bottom waters into the sediment. But together with $SO_4^=$ ions, Mg^{++} and Ca^{++} are also trapped in the mud. The amount of magnesium can be calculated as follows: at the complete reduction of sulfates of interstitial water, for 0.26 percent of sulfur there will be 0.13 percent magnesium (considering that only two-thirds of sulfur is combined with magnesium). This will constitute about one-third of the total magnesium contained in the interstitial water at the time of burial, which is equal to 0.4 percent of dry sediment.

If it is assumed that all of the magnesium produced as a result of the reduction of sulfates goes to form dolomite, there should be a decrease of magnesium content in the interstitial water in the amount of one-third as compared to its content in the bottom water. This differential alone could not create a strong influx of magnesium from the bottom water into the mud. Thus, deposition of 0.13 percent magnesium would give rise to only one percent of dolomite (that is, one percent on dry-weight basis). In addition, the amount of organic matter is so low in carbonate muds that it is doubtful that any appreciable reduction of sulfates could occur here. The depth of water above the sediment may be an important factor in the speed and completeness with which the processes are carried out.

Another possible reason for the influx of magnesium from bottom waters into the sediment would be the decomposition of organic matter by bacteria with generation of CO_2. As a result of this process first the alkalinity ($\Sigma\ HCO_3^- + CO_3^=$) would rapidly increase and then would decrease with loss of CO_2 from interstitial water of the sediment. With increasing alkalinity dolomite could reach a saturation value and precipitate. Removal of Mg^{++} in this manner could result in its additional influx from bottom waters. According to Strakhov (1956a, p. 20), this also could not create any appreciable influx of Mg^{++} from bottom waters because the amount of organic matter (generating CO_2) is negligible in the carbonate oozes. The process very likely would give rise only to: (1) individual crystals of dolomite, (2) rare and small spots (mottled dolomite), and (3) concretions. Yet, as pointed out by Strakhov (1956a, p. 20), average dolomitization of *spotty metasomatic dolomites* reaches 30–70 percent and much more in some instances. It would appear, therefore, that to create such diagenetic dolomitization as is envisioned by geologists, the above process cannot of itself fulfill the requirements.

Some geologists have suggested that the following reaction could explain diagenetic dolomitization:

$$2CaCO_3 + MgSO_4 = CaSO_4 + CaCO_3 \cdot MgCO_3$$

Valyashko and others (in Strakhov, 1956a, p. 20), however, found that this reaction would occur only in waters saturated with $CaSO_4$. In addition, in interstitial waters the $SO_4^=$ ion more or less disappears as a result of bacterial activity. Teodorovich (1955, p. 99) attributes the absence of dolomite in the deposits of Kara-Bogaz-Gol Gulf to the high content of $MgSO_4$: $CaCO_3 + MgSO_4 + 2H_2O = MgCO_3 + CaSO_4 \cdot 2H_2O$, and the second stage of the reaction ($CaCO_3 + MgCO_3 = CaCO_3 \cdot MgCO_3$) could not take place.

A study of the processes of diagenetic dolomitization should involve consideration of porosity changes. It is noteworthy that the replacement of calcite by dolomite involves a contraction of about 12–13 percent (Chilingar and Terry, 1954) if the reaction proceeds as follows: $2CaCO_3 + Mg^{++} = CaMg(CO_3)_2 + Ca^{++}$. That is, this contraction will occur if there is no additional precipitation of dolomite ($Mg^{++} + Ca^{++} + 2CO_3^= = CaMg(CO_3)_2$), and there is no subsequent compaction. As a result of contraction, certain avenues are opened which provide a means of migration of ions and escape of CO_2. This would seem to apply to those ions which are free to migrate in the liquid medium of interstitial water.

Although the findings of Skeats concern elevated reefs in the Pacific and Indian Oceans (1903) and the Triassic dolomitic reefs of the Tyrol (1905), the principles of diagenetic dolomitization which he observed may also apply in slightly different environments. In a later paper (1918) in which these principles were more clearly

stated, Skeats concluded that marine dolomitization took place in shallow water of 0–150 feet depth in the presence of abundant CO_2 under slightly increased pressure and in a porous limestone; the latter permitted free movement of magnesium-bearing water. The process proceeded under conditions of optima, with sufficient time for the reaction to be complete. Slow subsidence was considered essential.

Source of magnesium is not always known. Fairbridge (1950, p. 385) pointed out that

"there are . . . three recognized sources of $MgCO_3$-rich sediments in coral-reef rocks: primary organogenic secretion in shallow water; secondary inorganic enrichment from sea water, under reducing conditions below sea level; and secondary concentration under sub-aerial conditions. To these must be added the intertidal primary precipitation of $MgCO_3$ from sea water on the reef-flat under the specialized conditions of raised temperatures and pH (aided by photosynthetic production of CO_2 . . .), together with secondary enrichment in the same zone by alternate solution and reprecipitation."

Ultimate source of magnesium still remains a matter for conjecture, however. Weathering of igneous rocks, whether in the sub-aerial or sub-aqueous interface, might provide sufficient MgO which, upon union with CO_2 in the proper environment, could be introduced into carbonate ooze. Barth (1952, p. 71–72) notes that "magnesia is usually encountered in amounts from 0 to 25 percent; but in dunites it may attain 50 percent." It would be conjectural to compare the amount of magnesia introduced at present time into marine waters with that which very likely was introduced in the geologic past. Evidence is not directly available to ascertain if at times igneous activity, particularly effusive in nature, provided relatively copious amounts of magnesium-bearing solutions to the shallow, warm, marine waters. On the tidal-flat and epineritic zones, areally extensive deposits of volcanic ash relatively rich in minerals and rock fragments containing magnesia may have accumulated. Finely-divided particles, in particular, became part of the ooze and, attendant upon submarine weathering (halmyrolosis) and other physico-chemical processes operating in the interface, possibly provided additional Mg^{++} ions.

MECHANISM OF DIAGENESIS

Up to this point in the discussion, emphasis has been placed upon the possible method or methods of introduction of Mg^{++} ions into the carbonate ooze. Of equal, if not greater, importance in the process of diagenesis is an understanding of the mechanism of *removal of* Ca^{++} *ions*. The writers call attention to the studies of Frederickson (1951, p. 231–32) relative to mechanism of weathering. It is not assumed that identical conditions exist during the process of weathering as in the process of diagenesis, but rather that certain analogies are apparent. Frederickson visualizes the mechanism of weathering as "a process whereby the hydrogen ions of crystalline water are base exchanged for the sodium ions of albite (which is used as a model)." Thus, during dolomitization in the diagenetic stages, Mg^{++} ions are possibly base-exchanged for Ca^{++} ions through the crystalline network adsorbed on the unstable carbonate ooze. Now, in what manner do magnesium-rich solutions gain access to these carbonate sediments? Is it mass movement of solution only (such as through developed porosity), or by ionic diffusion? It could certainly not be a dry ionic diffusion (except as measured locally in millimeters). Holser (1947, p. 389) states that:

"A number of . . . authors . . . have pointed out the fact that diffusion through a fluid phase is a particularly convenient mechanism of transport in replacement, because it easily allows the movement of matter to the replacing front and away from it, within the same volume of fluid, each ion moving down its own concentration gradient. Furthermore, the precipitation of an ion at the replacement front automatically provides the impetus for further supply because removal decreases the concentration of that ion."

Is the replacement of limestone by dolomite during diagenesis a process analogous to the replacement of limestone by supergene minerals as tested by Garrels and Dreyer (1952)? That is to say, are the reactions of hydrolyzed, slightly acid solutions essentially volume-for-volume with duplication of textures? Access of magnesium-enriched solutions can be a function of secondary permeability (that is, formed in a late stage of diagenesis), and may be very important in the formation of diagenetic

dolomites. Movement outward (that is, into the magnesium-impoverished areas) from secondary openings (secondary porosity) most likely is by diffusion, not forced flow. Experiments conducted by Duffell (1937), and ones by Garrels, Dreyer, and Howland (1949) considered this "free diffusion," which is defined as the rate at which a small but finite concentration front moves outward from the reservoir of higher concentration. The transfer of material is accomplished entirely by relative movement of solute and solvent.

The crux of most of the problem of diagenetic dolomitization is concerned, so the present writers believe, with the intergranular spaces connected to the pore spaces which are developed during dolomitization. The porosity developed during the change of calcite or metastable aragonite to dolomite is probably sufficient to provide necessary diffusion centers from which concentrations of Mg^{++} ions can migrate into and through the adsorbed crystalline water surrounding the Ca^{++} ions. This porosity comprises the reservoirs into which the solute with solvent can move (such as from bottom waters and connate waters) to serve as the distributing centers for continuous diagenetic dolomitization.

As the diagenetic replacement by dolomite progresses, the impoverishment of interstitial waters (in the pore spaces and intergranular film) in magnesium content would thus enable an additional influx of Mg^{++} ions from bottom waters. Some porosity which might result from secondary dolomitization could furnish additional space.

Assuming that the above premises are correct for present conditions, and possibly were much the same in the geologic past, the question logically arises: "How do the Mg ions move to the remainder of the carbonate ooze?" Possibly this is accomplished in the majority of diagenetic dolomites through the intergranular film. This film, long considered by many as an important avenue through which ions are transferred—in the presence of water—during granitization of sediments, can suffice as a means of distributing the Mg^{++} ions through a lime ooze. This intergranular film is exceedingly thin, and surrounds grain boundaries in a somewhat disarranged manner; free motion of ions is to be expected. This is of utmost importance because rigid limitations are not placed on distance of migration of Mg^{++} ions in, and Ca^{++} ions out, relative to the porous zones (distributing centers) previously developed. Garrels, Dreyer, and Howland (1949) have demonstrated the importance of directional porosity during diffusion of ions through intergranular space in limestone under experimental conditions, and estimate "the *maximum* distance of penetration in 1,000,000 years of an active concentration front of any ion into any rock at 100° C gives a value of approximately $2\frac{1}{2}$ miles."

Figure 3 is a schematic diagram illustrative of the writers' concept of what relationships may exist in and near the intergranular film.

A complete evaluation of the role played by catalysts cannot be given here, but it is worthy to note the following systems of equilibriums (presented in abbreviated form):

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons \underbrace{Ca(HCO_3)_2,\ Mg(HCO_3)_2}_{\text{in solution}}$$

$$\rightleftharpoons \underbrace{CaCO_3\downarrow,\ MgCO_3\downarrow,\ CaMg(CO_3)_2\downarrow}_{\text{precipitate}}$$

The reaction goes to the left in the initial stages of diagenesis (due to evolution of CO_2), as a result of the activity of bacteria and decomposition of organic matter. As aragonite or calcite change to dolomite, avenues of increased porosity will enable CO_2 to escape and thus carbonates will precipitate. The resultant ooze—a mixture of Ca^{++} and Mg^{++} ions in an unstable crystalline water meshwork—would possibly have the optimum conditions conducive to diagenetic dolomitization. It is not necessary that all dolomite forms by replacement during diagenesis; it forms also by direct precipitation as the interstitial waters become saline and saturated (with respect to dolomite). According to Strakhov (1956a, p. 18), some dolomite could also precipitate during the sedimentation stage and later be redistributed during the diagenetic stage, sometimes giving a spotty appearance to dolomitic limestones. Some dolomite might form from the interaction of $CaCO_3$ with some $MgCO_3$ salts (probably not as $MgCO_3$, however, but as $xMgCO_3 \cdot yMg(OH)_2 \cdot z2H_2O$).

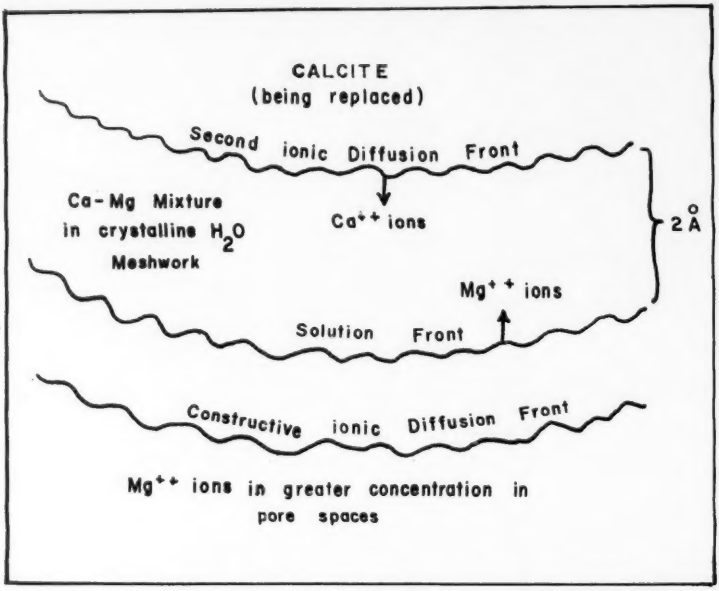

FIG. 3.—Highly enlarged view of intergranular film—hypothetical.

According to Strakhov (1956b, p. 199), the increased dolomitization due to secondary removal of $CaCO_3$ (an epigenetic process) does not seem to be important. For example, in one cubic decimeter of limestone with 5 percent dolomitization and sp. gr. of 2.7, there would be 13.5 g of dolomite. Creation of 10 percent porosity would necessitate the removal of 27 g of $CaCO_3$ from each 270 g of rock; and consequently the dolomitization of the remaining mass would be:

$$100 \times \frac{13.5}{270-27} = 5.5 \text{ percent.}$$

In other words, it will increase by a negligible amount—only 0.5%. Increase of porosity to 20% will give an increment of dolomitization of 1.2%; to 30%–2.1%; to 40%–3.3%; and to 50%–5.0%. In the latter case, the rock would have a sponge-like appearance, yet the percent dolomitization would increase by 5% only. This concept, however, applies to epigenetic processes only (not diagenetic); it is given here because secondary removal of $CaCO_3$ is frequently used to explain increased dolomitization.

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REFERENCES

BARTH, T. F. W., 1952, Theoretical petrology. John Wiley & Sons, Inc., New York, 387 p.

CHILINGAR, G. V., 1956a, Note on direct precipitation of dolomite out of sea water: The Compass of Sigma Gamma Epsilon, v. 34, p. 29–34.

———, 1956b, Relationship between Ca/Mg ratio and geologic age: Am. Assoc. Petroleum Geologists Bull., v. 40, p. 2256–2266.

CHILINGAR, G. V. AND TERRY, R. D., 1954, Relationship between porosity and chemical composition of carbonate rocks: Petroleum Engineer, v. 26, p. 341–343.

DUFFELL, S., 1937, Diffusion and its relation to ore deposition: Econ. Geology, v. 32, p. 494–510.
FAIRBRIDGE, R. W., 1950, Recent and Pleistocene coral reefs of Australia: Jour. Geology, v. 58, p. 330–401.
———, 1957, The dolomite question (*in:* Regional aspects of carbonate deposition): Soc. Econ. Paleontology and Mineralogy, Special Publication No. 5, p. 125–178.
FREDERICKSON, A. F., 1951, Mechanism of weathering: Geol. Soc. America Bull., v. 62, p. 221–232.
GARRELS, R. M., AND DREYER, R. M., 1952, Mechanism of limestone replacement at low temperatures and pressures: Geol. Soc. America Bull., v. 63, p. 325–380.
GARRELS, R. M., DREYER, R. M., AND HOWLAND, A. L., 1949, Diffusion of ions through intergranular spaces in water-saturated rocks: Geol. Soc. America Bull., v. 60, p. 1809–1828.
HOLSER, W. T., 1947, Metasomatic processes: Econ. Geology, v. 42, p. 384–395.
KAZAKOV, A. V., TIKHOMIROVA, M. M., AND PLOTNIKOVA, V. I., 1957, System of carbonate equilibriums (dolomite, magnesite): Trudy Inst. Geol. Nauk., Akad. Nauk SSSR, Geol. Ser., No. 64, Vypusk 152, p. 13–58. (Available from George V. Chilingar.)
NEWELL, N. D., AND RIGBY, J. K., 1957, Carbonate deposition on the Great Bahama Banks (*in:* Regional aspects of carbonate deposition): Soc. Econ. Paleontology and Mineralogy, Special Publication No. 5, p. 15–72.
SKEATS, E. W., 1903, The chemical composition of limestone from upraised coral islands, with notes on their microscopical structures: Harvard Coll. Mus. Comp. Zoology Bull. 42, p. 53–126.
———, 1905, The chemical and mineralogical evidences as to the origin of the dolomites of southern Tyrol: Geol. Soc. London Quart. Jour., v. 61, p. 97–141.
———, 1918, The formation of dolomite and its bearing on the coral reef problem: Am. Jour. Sci., 4th ser., v. 45, p. 185–200.
STRAKHOV, N. M., 1953, Diagenesis of sediments and its significance for sedimentary ore formation: Akad. Nauk SSSR Izv., Ser. Geol., no. 5, p. 12–49.
———, 1956a, Types and genesis of dolomite rocks (*in:* Types of dolomite rocks and their genesis): Akad. Nauk SSSR Izd., Trudy Geol. Inst., Vypusk 4, p. 5–27. (Available from Harold J. Bissell.)
———, 1956b, Distribution and genesis of upper carboniferous dolomite rocks of Samarskaya Luka (*in:* Types of dolomite rocks and their genesis): Akad. Nauk SSSR Izd., Trudy Geol. Inst., Vypusk 4, p. 185–208.
TEODOROVICH, G. I., 1955, Towards the question of formation of sedimentary calcareous-dolomite rocks: Trudy Inst. Nefti, Akad. Nauk SSSR Izd., Tom 5, p. 75–107. (Available from George V. Chilingar).

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FIGS. 1–3, DECEMBER, 1958

COPROLITES: A REVIEW OF THE LITERATURE AND A STUDY OF SPECIMENS FROM SOUTHERN WASHINGTON[1]

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ABSTRACT

The term coprolite was found to be defined in many different ways, and this led to a review of the pertinent literature on the subject, with special reference to composition, origin, and geological significance of these petrified animal excrements. This review includes 63 references.

Coprolites from southern Washington, collected from the bed of Salmon Creek, range from 0.5 to 10 cm in diameter. Their mineralogical and chemical composition was established by microscopic, chemical, X-ray and spectrographic analyses, and found to be almost exclusively siderite with traces of limonite. We thus have a perfect example of complete replacement, since the shapes do not leave any doubt as to their true animal excrement origin.

INTRODUCTION

In preparation for a study of coprolite specimens collected in southern Washington, a search of the literature on coprolites was made. Because no comprehensive treatment was found in any one reference, a review of the literature is given as the first part of the present paper.

The results of studies of the specimens from Washington are reported and discussed in the second part of the paper.

REVIEW OF THE LITERATURE ON COPROLITES

Definitions of the Term "Coprolite"

Webster's New Collegiate Dictionary defines the word coprolite as "fossil dung." Its etymology is Greek and comes from the two words *kopros* which means dung, excrement, and *litos* which means stone, rock. In German the term is "Koprolith" and in Spanish "coprolito." Geologically speaking, coprolites are petrified excrements of animals living during the time a rock formation was deposited. The definitions and descriptions taken from the literature show some discrepancies as to the size and nature of products named coprolites. The following paragraphs list some of the more important definitions. None of the descriptions found in the literature so far report the first use of the term coprolite. The oldest references found are Dekay's two papers on coprolites of North America, of 1830.

Grabau and Shimer (1910, p. 828) also define coprolites as "the fossil excrements of animals."

In Dana-Ford's Textbook of Mineralogy (1932), coprolites are defined as being "impure calcium phosphate." No occurrences or examples are mentioned and neither is the fact stated that coprolites may be silicified or carbonatized. The earliest reference on silicified coprolites found so far is from Dana (1895, p. 785). Dana reported on Jurassic Saurian coprolites which are sometimes silicified.

The definition and description given by Schuchert and Dunbar (1937, p. 10) is very general and does not imply any restrictions as to the size: "Fossil excrement constitutes another class of fossils known as *coprolites*. These often contain the scales of fishes and other hard parts of animals that have been devoured. Wherever associated with skeletal remains in such a way that their source can be recognized, coprolites are of special significance for the light they throw on the food and feeding habits of the animal in question. For example, the dried dung found with fossil groundsloths at two localities, one in South America and the other near El Paso, Texas, gives the only proof we have of the type of vegetation preferred by that race of extinct monsters."

Twenhofel (1932) states in his "Treatise on Sedimentation" (p. 152): "The excreta are mostly in the form of pellets, and these seem to be extremely abundant over many parts of the sea bottom. Vaughan states

[1] Manuscript received January 27, 1958.

that the ellipsoidal bodies described by him in 1924 are castings of mud-feeding organisms and he also thinks that the ellipsoidal aggregates described by Thorp as composing a considerable part of the "coprolitic mud" are castings of mud-eating organisms" (Vaughan, 1924; Thorp, 1931).

Whereas Pettijohn (1949, p. 161) states that "Coprolites are a relatively uncommon constituent of sediments," Twenhofel thinks that they can be considered a major constituent of certain sediments: "With several authorities considering that nearly all marine deposits pass through the intestinal tracts of organisms and that the major portions of marine deposits are excretions, and it being certain that such action is extensive, it follows that the modification of sediments by organisms has tremendous significance" (1932, p. 152). This discrepancy in opinion originates mainly from the different way of defining the term coprolite.

On pages 284-285, Twenhofel (1932) mentions, under the heading of calcitic limestones, another interesting observation on coprolites: "A feature observed in several seemingly pure calcitic limestones is the presence of ellipsoidal particles of the order of magnitude of small oolites. These are composed of clay and broken calcite fragments and are interpreted as coprolitic." No example or reference is given for this type of coprolite. In his "Manual of Geology," Dana (1895) defines coprolites as "isolated excrements in rocks" (p. 73), and gives (on the same page) six analyses of nonsilicified coprolites from four localities. They contain mainly calcium phosphate and calcium carbonate. some organic material and varying amounts of silica, magnesium carbonate, iron sesquioxide, alumina, water, lime, and sodium chloride.

Twenhofel and Shrock (1935, p. 19) state: "The term *coprolite* or *castings* has been applied to fossil excreta; hence the composing material has passed through the alimentary tract of some individual. In many cases the excreted matter has undergone physical and chemical changes and for these reasons stands out conspicuously on weathered surfaces. Coprolites may be in the form of straplike marking, discrete pellets, or an alternating series of markings and pellets. Fish coprolites found in the Devonian of New York contained ganoid scales, showing that the animal fed on that particular kind of fish"; and, on page 137, these authors say: "Modern sea bottoms contain many excremental or *fecal pellets.* Some of these are known to have been made by worms. Certain small fossilized spherical bodies, referred to as *coprolites* or *castings,* may have been formed by worms in the same manner. In some instances their origin seems fairly clear (fig. 43A), but often there are no known means of determining how they were formed."

K. von Bülow (1941) uses the term "Koprolithe" only for the excrements of saurs: "Als Phosphate werden zu Düngezwecken ebenfalls die in manchen Gegenden und Schichten häufigen *Koprolithen* gewonnen, das sind die versteinerten Exkremente von Sauriern" (p. 120). On page 205 (fig. 272) Bülow pictures three coprolites of upper Triassic age, which however, do not show very typical shapes. Without mentioning the term coprolite, Williams, Turner and Gilbert (1954, p. 348), say that "in some limestones, for example, the finest-grained, darkest portions of the rock are ovoid bodies, and the rock is termed *pellet limestone;* thin sections of these are mottled by dark, indistinctly bounded oval patches in a cement of clearer and slightly coarser calcite" (their fig. 122B). "The ovules may represent fecal pellets of organisms that lived in the lime muds when they were being deposited. They have been called *pseudo-oolites* because they superficially resemble oolites except they are structureless."

Pettijohn (1949) assigns the term coprolite only to "larger structures ($\frac{1}{2}$ to 6 in. in length)" whereas he calls faecal pellets or organic excreta "those of simple ovoid form and of small size—1 mm or less in length" (p. 160). Here is his definition (p. 161): "*Coprolites,* of origin analogous to that of faecal pellets, are larger structures ($\frac{1}{2}$ to 6 in. in length) and are characterized by light to dark-brown or black color, ovoid to elongate form, and surface marked by annular convolutions. Longitudinal striae or grooves are rarely present. The brown vitreous material of many coprolites is phosphatic—optically isotropic and with refractive index near that of cellophane (1.58–1.62). Bradley (1946) has shown that the coprolites of the Bridger Formation are probably a carbonate—apatite (francolite).

Coprolites are a relatively uncommon constituent of sediments."

Ladd (1957) writes: "Coprolites is a general term that includes a variety of nodular phosphatic masses believed to be the fossilized excrement of animals," (p. 20).

Thus, some authors make no difference between fecal pellets and coprolites whereas others call the small fossil excrements fecal pellets and the larger excrements coprolites. It does not seem that such a differentiation has any advantage, since the difference is only a gradual one. (The two spellings of fecal and faecal are used and both are correct. The word originated from the Latin term faex, faeces which means dregs.)

Considering such facts as the huge deposits of guano (for example on the Peruvian and the Chilean coasts) and the extent of saurian coprolites used as fertilizers, coprolites may well be considered a wide-spread constituent of sedimentary rocks. Moreover, probably the bulk of all phosphate deposits was formed by deposition or reworking and deposition of animal excrements (and bones). Although most of these deposits no longer exhibit the shapes of excrements, they prove the importance of this type of sedimentation. (Brief, up-to-date reviews of the phosphate deposits of the world were given by Bateman, 1950, p. 174–175, and p. 812–818, and P. Niggli, 1952, p. 454–458. The U. S. Atomic Energy Commission is carrying out extensive studies of the Phosphoria Formation in Idaho and other western states and has published a number of very detailed stratigraphic sections. See Geological Survey circulars nos. 260, 262, 324–327.)

Geological Significance

Just like other fossils, coprolites may serve as marker-fossils, if they are typical of a definite geological horizon. According to Shrock (1948, p. 185 and 304) coprolites can be used for determination of bottom and top of vertical, folded, or turned-over sedimentary units. He states (p. 185–186): "Animals that eat the materials of a bottom excrete pellets of many kinds known as 'coprolites,' 'castings,' 'fecal pellets,' etc. These excreta, being soft and more or less unconsolidated at the time of deposition, tend to become cemented to the substratum during consolidation. When they are buried the layer covering them has groovelike counterparts, and when the contacting layers separate, the coprolites adhere to the surface on which they came to rest, thus indicating the top of the sequence." In his figures 146 and 147, Shrock pictures two good examples of coprolites which, on separation of the strata, adhered to the surface on which they came to rest.

Some Occurrences Cited in the Literature

In the natural sciences investigations into a virgin field have to begin with an inventory of facts and observations. It is hoped that the following list of references, which is such an inventory, will not only illustrate the role of coprolites in sedimentary petrology and the occurrence of these fossils in time and space, but will also serve as a basis for further sedimentological, mineralogical, geochemical, and paleontological studies of fossil excreta. The chronological listing of individual references was preferred to a mere tabulation of authors, locations, etc., in order to point to some interesting details.

Nicholson (1889, p. 21) mentions the phosphate problem, which consists of the interpretation of many phosphatic beds, lenses and nodules as "products of vital action," essentially as petrified excreta of fishes, reptiles, and mammals (true "coprolites").

Dana (1895) lists the following localities; Bourdiehouse, Fifeshire, Koschtitz, and Oberlangenau. Some authors are mentioned but neither the references nor the exact localities are given. On page 567 Dana mentions coprolites from the upper Silurian: "Fishes, containing fragments of the shells of the Mollusks and Crinoids on which they fed." On page 754 he mentions that coprolites from Jurassic crocodilians "are common on the shales at Phoenixville, Pa." On page 785, dealing with Jurassic saurians he says: "The Coprolites (fossil excrement) of the saurians are not uncommon; one is represented in figure 1322. They are sometimes silicified and, notwithstanding their origin, are beautiful objects when sliced and polished." This figure mentioned is from Buckland and is very similar to the specimen in the upper right of figure 1 of the present paper.

Merrill (1897, p. 152) gave the following definition of coprolites: "*Coprolite nodules* are likewise the excrements of vertebrate animals; those among the Carboniferous shales of the basin of the Firth of Forth are regarded as accumulated excretions of ganoid fishes."

Dacque (1928) mentions coprolites as useful indicators of animal life in certain horizons and pictures in fig. 20 a worm coprolite.

Fikentscher, R. (1933) writes about coproporphyrin in crocodile coprolites from Eocene lignite of the Geisel Valley, Germany.

Bayer, B. (1934) saw coprolites in Paleozoic sediments near Plzen, Czechoslovakia.

Cayeux, L. (1936) described coprolites of the North African Phosphates.

Augusta, J. (1936) found a stegocephalian coprolite from the Permian of Moravia, Czechoslovakia, which he pictures in one figure, and fish coprolites from the Cretaceous beds at Kladno (1938).

Trusheim, F. (1937) from the contents of Nothosaurus coprolites, drew conclusions on the food of these animals. He found remains of the ganoid fish Gyrolepis albertii, found in the spinosa beds of the Muschelkalk Formation (Triassic) of the Würzburg region, Germany.

Wetzel, W. (1937) describes coprolite admixtures in marine sediments, chiefly Tertiary, and their effect on the constitution of the sediments, particularly in the formation of glauconite and phosphates.

Firtion, F. (1938) describes coprolites from the lower Liassic of Alsace-Lorraine, France.

Rogers (1938; ref. Ladd, 1957, p. 21) found pellets excreted by termites in fossil wood in the Pliocene of Santa Barbara County, California. Both the wood and the pellets, which partly fill irregular areas where the cell structure of the wood is absent, are opalized.

Richter, R. and E. (1939) found coprolites in the Ordovician of the Rhine region and Bohemia which may prove to be of use as an index fossil.

Takahashi, J.-I. (1939) concluded in his synopsis on glauconitization that glauconite may also originate from fecal pellets, and that the presence of organic matter seems to facilitate glauconitization.

Bjørlykke (1941) defines coprolites in his note on phosphorite. On page 211 he mentions Ichthyosaurus and Plesiosaurus coprolites.

Beyer, K. (1941) found coprolites (Tomaculum problematicum) in the Ordovician in three localities of the Ebbe anticline, Sauerland, Germany, which are index fossils for the upper Llanvirn and, in some cases, the lowermost Llandeilo of Sauerland. The same author found (1944) some new Ordovician Tomacula problematica in Sauerland.

Wagenbreth, O. (1942) found coprolites in nodular dolomites considered equivalent to the Kupferschiefer (Permian).

Brown and Salter (Wetmore, 1943, Ladd, 1957) recovered a coprolite containing the impressions of numerous feathers. This coprolite which was probably from a large fish or crocodile, occurred in the marine Miocene beds of Maryland.

Bradley, W. H. (1946) described some remarkably well preserved mammalian and reptilian coprolites from the Eocene Bridger Formation of Wyoming and indicates their siliceous composition and well preserved micro-organisms. The feces fell on dry ground and were soon covered by volcanic ash, which yielded the siliceous waters responsible for the silification.

Parejas (1948) described three new species of coprolites from Jurassic and Oligocene localities in France and Turkey, closely resembling the fecal pellets of living thalassinids.

Shrock mentions (1948, p. 187 and p. 305) the Triassic Rhaetic bone beds of England, the thinly laminated Kokomo Limestone of Indiana, and the Green River Shale of the Western United States.

Visse (1950) found no significant difference betweeen the analyses of the coprolite fraction and the pseudo-oolitic fraction of Eocene phosphate beds of Algeria.

Donze (1950) made the interesting observation that, although crustacean fossils are rare in upper Jurassic deposits of the Princes and Chambotte Mountains in the Savoien Jura, France, crustacean coprolites occur abundantly.

Hutchinson (1950, p. 458; ref. Ladd, 1957, p. 21) "reviewed described occurrences of the fossilized dung of the cave hyena in England and on the Continent. In one of the continental occurrences the hyena droppings formed two definite layers between two

human occupation levels."

Rankama and Sahama (1950) call their seventh geochemical subdivision "coprolites or biolites."

Dietrich (1951) described excrements, probably of some carnivorous mammal, and indicated that the shapes and the phosphate content distinguishes these definitely from concretions.

Brotzen (1951) determined phosphoritic concretions in Mesozoic and younger sediments to be annelid coprolites.

Mayer (1952) creates two new coprolite species for wormtube fillings consistently largely of fecal pellets.

Bonorino and Terrugi (1952) give Spanish definitions of the words "coprogeno" and "coprolito," without referring to the alternative term, fecal pellets.

Moret (1953, p. 8) mentions coprolites, "dejections," as one of the fossil signs of animals.

Willcox (1953) gave a description and discussion of the possible origin of six types of coprolites found in upper Cretaceous phosphatic chalks of four localities in Southeast England.

Cuvillier (1954) cites coprolites from Mesozoic beds in France and North Africa.

Abelson (1957) presented an account on organic constituents of fossils and referred on p. 87 to Fikentscher's (1933) description of porphyrin from coprolites of Eocene crocodiles.

Kornicker and Purdy (1957) give a brief account of Bahamian coprolites, with one excellent microphotograph.

As can be seen from these references which represent, of course, only the beginning of a bibliography on coprolites, these petrified animal excrements are known from many localites as well as from the Paleozoic, Mesozoic, and Tertiary.

COPROLITES FROM SOUTHERN WASHINGTON

Occurrence

The coprolites described in this paper were found in the bed and on the bank of Salmon Creek in Lewis County, Washington, U.S.A., a few miles south of Toledo. This creek is a tributary to the Cowlitz River, which in turn flows into the Columbia River. The rocks traversed by Salmon Creek include basaltic and andesitic flows and shaly and sandy sediments of Tertiary to Recent age. The coprolites in the locality studied are fairly abundant. In a place only a few hundred yards from where Highway 99 crosses the river, more than fifty coprolites were found in an area of about 200 square yards.

Description

The size of the coprolites ranges from 0.5 to 10 cm in diameter. The shapes are varied. Many coprolites do not show shapes which, at a first glance, tell their excrementary nature. They could be taken for a common pebble of some dark brownish rock. Their hardness and usually also their pitted, slightly undulatory surface reveals, however, their true nature. Many specimens are clearly dung-shaped and leave no doubt as to their origin. The most typical ones have been selected and photographed (fig. 1).

FIG. 1.—Four samples of coprolite from Salmon Creek, southern Washington. Colors: Dark brown to reddish brown; in grooves often brownish-yellowish "clay-color." Note the striations and congestions. Scale is in cm.

The color is usually dark brown and, if it were not for the hardness, they could be taken for true excrements.

Under the microscope the same observations could be gained from all four thin sections prepared. They reveal a fine grained mosaic of generally isometric, colorless or limonite-colored, anisotropic crystals. The refractive index is clearly higher than that of Canada-balsam. The largest crystals are with one exception (see later) only 15 microns in diameter. The average diameter is, however, 5–10 microns. There are no crystal forms visible with exception of a few crystals exhibiting rhombic cleavage. The over-all structure of the mosaic displayed in the thin section is very similar to the mosaic formed by the periclase crystals in magnesite bricks.

The limonitic pigmentation is arranged in the following way: in all four sections a dark brownish-reddish crust is present. In one spot of a dark sample a group of large crystals, 30–40 microns in diameter, was observed just inside this crust. In the interior, two samples have an even distribution of limonite. About 90 percent of the mosaic crystals contain limonite pigment and only about 10 percent are more or less free. The two other samples reveal in their interior portions a fine, mostly loose, and pseudo-fluidal network of limonite streaks or clouds (partly intergranular skins).

With HCl 1:10 no reaction was observed on any of the four samples. With HCl conc., however, the three samples showing whitish-yellowish-green spots exhibited slight effervescence, producing a honey-yellow solution.

A study of a powder sample revealed that the bulk of the material is siderite, to a great extent pigmented by limonite inclusions or limonite films on the surface. On clear grains the refractive index of 1.65–1.88, and a birefrigence of 0.2 could be determined. There are also present a few fibrous crystals of chalcedony ($N = 1.53–1.54$, fibers elongated normal to C) which may vary in structure in such a way as to cause extinction angles of about 45°. There are other minerals present, but only in small traces which do not allow a safe determination. The over-all hardness of the specimen varies between 5 and 7 (Mohs).

According to the observations in thin sections, on ground samples, and in a polished section, both α- and γ-limonites occur in these coprolites. The α-limonite (Nadeleisenerz Samtblende), $HFeO_2$, in which H is present as cation, shows yellowish-brownish color and forms 99 percent of the limonite present. On the polished surface it has low reflectivity. The γ-limonite (Rubinglimmer) (FeO(OH), shows up in very few particles of the ground sample, exhibiting the typical ruby-red colors.

The polished section shows a marked zoning. The rim of the specimen consists of about 80 percent siderite grains in a matrix of limonite, whereas the center consists of about 90–95 percent siderite surrounded by intergranular films of limonite. In a few places where the siderite crystals are rather large they exhibit good idiomorphic cross-sections. In the border zone the siderite has dark brown colors (from the reflection of the surrounding limonite) whereas in the central portion the coloring is only slight (yellowish-light brown tinges).

The limonitic matrix of the outer zone is crossed by streaks or veinlets of a mineral with higher reflectivity (15–25 degrees). Some of this material (with reddish-brown interior reflections) may be lepidokrokite (γ-limonite, Rubinglimmer), some may be hematite (strong reddish reflections). A few very small grains of pyrite (5–10 micron diameter) are scattered throughout the crust and some fairly large spots (50–100 micron diameter) of pyrite or marcasite are present in the central portion (these are difficult-polishing, and probably are of colloidal origin). Other very small and scarce grains are probably magnetite and one grain is chalcopyrite (10 micron diameter). Some or all of these sulfides may have been picked up from the lead lap during polishing.

X-ray Mixture Analysis of Two Coprolite Samples

Two samples of coprolite were analyzed by the X-ray mixture analysis of powdered material (see fig. 3). Sample no. 1 is a dark reddish-brown portion of a typical border zone, cut from the outermost left corner of the upper left sample pictured in figure 2. Sample no. 2 is a whitish-green central portion with only traces (about 5 percent) of reddish material. It was cut out of the center of the sample pictured in the lower left of figure 2.

FIG. 2.—Macro-section through four specimens of coprolite from Salmon Creek. Most of these coprolites exhibit a definite zoning produced by a difference in limonite-hematite content. The colors are as follows: dark grey (outer zones) = dark reddish-brown. Lighter grey (intermediate zones) = light reddish-brown. Whitish, mottled interior portions = greenish-grey. The outside is often covered by a yellowish-reddish (soft, clay) or a grey (hard) thin crust. (0.01–0.5 mm)

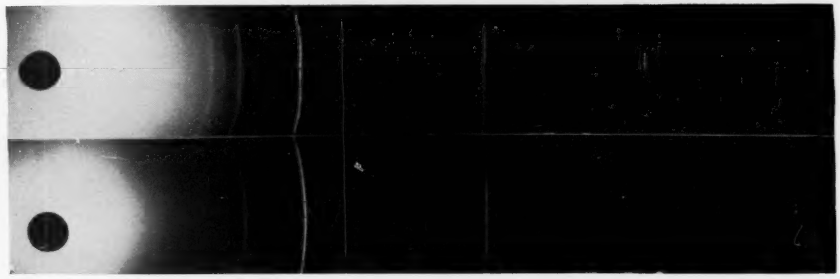

FIG. 3a. (upper part).—X-ray powder photograph of a typical border zone of a coprolite pictured in figure 2 (outermost left corner of the upper left sample). It shows only strong lines of siderite with very slight bands of α-limonite.

FIG. 3b. (lower part).—X-ray powder photograph of a whitish-grey central portion with only traces of reddish material. (Center of the sample pictured in fig. 2, lower left.) This photograph shows only siderite lines. Both of these X-ray power photographs were taken with Cr-K-radiation, using the Debye-Scherrer method and a camera with 114 mm diameter.

A test of six specimens with the Geiger counter was negative. The number of kicks did not go above background intensity (as far as was noticeable by ear phone). A test with ultraviolet light was negative also.

Spectrographic Analysis

The spectrographic analysis was made on two portions of the same sample (fig. 2, lower left). The first portion consists of the dark brown rim, and the second portion was cut out of the center and contains 92–95 percent whitish-grayish-green and only 5–8 percent reddish material which could not be separated from the light portions.

A magnetic test with a small hand magnet removed only one particle (out of at least 1000) from the medium-grained crushed reddish-brown crust and only a few from the light center portion. It is believed that these very small grains reacting to magnetism are partly iron splinters from the crusher and hammer and, in the center portion, they partly may be traces of magnetite. The results of the semiquantitative spectrographic analysis are:

Major constituents (probably over 10%):	Fe
Minor constituents (probably 1–10%):	—
Strong traces (probably .1–1.0%):	As, Si
Weak traces (probably 0.01–0.1%):	Cu, Ca
Very weak traces (probably less than 0.01%):	Sb, Pb

The Origin of the Washington Coprolites

An interesting note on the occurrence and origin of Washington coprolites from the same locality was published by D. M. Major in 1939. Major pictures 17 specimens. According to him they may also consist of "oxides of iron, hematite and limonite, plus an infiltration of silica." He found "that associated with the 'coprolites' of Lewis County is the mineral vivianite, an iron phosphate found in rather large amounts, but not as plentiful as the rope-like masses." This raises the question whether the carbonatized coprolites consisted, previously, of calcium phosphate, a common constituent of coprolites. "Tests made by the United States National Museum," Major reports, found that the Washington coprolites "consist largely of an iron mineral—siderite."

With reference to the origin, the only published account I found is again in Major's popular article: "In the October 1935 issue of The Mineralogist Magazine, H. C. Dake suggested the theory that the Lewis County 'coprolites' were of stalactitic origin. Dake accounted for the peculiar twistings of the stalactites (?) on the basis of changing air currents through the caverns in which the 'coprolites' may have had their origin."

Major rejects the "animal theory" and proposes a "fossil theory." Despite a keen eye for details he did not see the possibility that a "fossil animal theory" might be another possibility. He writes: "Practically every specimen found in the Salmon Creek area has a somewhat flat base, perhaps the point at which it was attached to something else. This and the general form of the specimens suggests a coral or a Bryozoan sea moss. . . . Each in dying left its minute skeleton and upon it others built a reniform aggregation of lime. As time went on the little colony broke from the reef and became buried in the decaying vegetation of a tropical swamp. In the swamp percolating solutions and iron depositing bacteria came into action to remove the calcite and replace it with iron minerals, finally resulting in what can be termed fossil pseudomorphs."

This account by a non-professional is remarkably good. Concretionary nature was suggested orally even by professionals. As mentioned, a careful study of the possibilites of origin has been made and special papers on concretions and pseudofossils were consulted; for example, the paper on pseudofossils by Wolansky (1956). Besides concretions, gastroliths and otoliths might also be mistaken for coprolites. Yet, the following criteria make it reasonably definite that we are dealing with fossil mammal dung: "I believe there is no doubt whatever but that some of the specimens, and perhaps most of them, are coprolites . . . I could detect no organic microstructure, or any other kind of structure in these thin sections. Nevertheless, I am convinced from the extraordinary fine external form and markings that many of these objects are coprolites. All the internal structure seems to have been destroyed by crystallization of the carbonate." (W. H. Bradley, personal communication, June 25, 1957.)

Following is the list of criteria which make it most probable, if not certain, that the Washington coprolites are of dung origin.

Maybe none of them would be entirely conclusive if taken alone; however, together they are strong evidence:

Criteria for excremental nature:

1. The extrusion forms. There does not seem to be any process in geology which can produce extrusion shapes of this size and form—except excrementation. Concretions do not have a frequently congested curvature on one side of the individual segments. These congestions appear to be on the side of deposition.
2. A flat base on the side of deposition which was already described by Major 1939).
3. Striations, typical for extrusion from the great gut of mammals.
4. The constantly limited length or quantity, typical for excrements. This would be an astonishing, unusual feature for concretions, particularly since there are no exceptions.
5. The variation of shape corresponds to the variation of "viscosity" as known from excrements.
6. Some forms correspond to the form of the great gut of mammals and were probably extruded as hard excrements.

Whether these coprolites from Washington should be erected to a new species or not has to be decided by a paleontologist. Coprolites can be more or less petrified. The petrification has most probably taken place during lithification of the surrounding rock unit. The coprolites from Salmon Creek were found in situ, contained in the volcanic ash or the shaly-sandy sediments (containing much volcanic material) occurring in upper portions of Salmon Creek, and in the gravel.

One of the most remarkable features of the coprolites described in this paper is, as mentioned, the perfect and complete replacement of the original material. It is reasonable to assume that this replacement was pre-diagenetic. It thus took place before consolidation, which means that the solutions could move around freely, the mobility of the materials involved was great and it is not necessary to think in terms of diffusion along intergranular films or diffusion in a solid state. Holser (1947) has pointed to many difficulties involved in a post-diagenetic replacement.

In a previous paper I described pseudomorphs of fluorite crystals from the same region (1952, p. 334). These fluorite crystals have also undergone complete replacement. The siliceous solutions causing this replacement originated probably from volcanic exhalations and ash, or both in the way stated by Murata (1940). Silicified woods are common in volcanic areas (Murata, 1940; Amstutz, 1954, p. 202). Sabbatoni (1920) was able to produce complete replacement of organic material in the laboratory by applying potassium permanganate, to produce manganese oxide replacement of the organic compounds. The carbonatizing solutions which replaced our coprolites may also have originated from volcanic sources. It remains to be seen how the replacement mechanism took place.

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REFERENCES

Abelson, P. H., 1957, Organic constituents of fossils: Geol. Soc. America Memoir 67, p. 87–92.
Amstutz, G. C., 1952, Replaced flourite crystals: Schweizer. min. pet. Mitt. 32, p. 334–337.
———, 1954, Versteinerte Wälder: Leben und Umwelt. Juni, p. 202–205.
Augusta, J., 1936, Ein Stegocephalen-Koprolith aus dem mährischen Perm. Zentr. Miner. Abt. b, no. 8, p. 334–337, 1 fig.
———, 1938, O rybich koprolitech z kladenské kridy (on fish coprolites from the Cretaceous beds at Kladno-Príroda (Nature), Brno, r. 31, c. 6, p. 173–176.
Bateman, A. M., 1950, Economic mineral deposits: 2nd Ed. John Wiley and Sons Inc., New York.
Bayer, B., 1934, Koprolity z kounovskych vrestev no Plzensku. Príroda, Brno, r. 27, c.1, p. 21–22.

BEYER, K., 1941, Zur Kenntnis des Silurs im Rheinischen Schiefergebirge I; Das Auftreten von Tomaculum problematicum Groom im Ebbe-Sattel und die Bedeutung der Kotpillen-Schnur für die Gliederung des sauerländischen Ordoviciums: Reichsstelle f. Bodenforschung. Ib. Bd. 61, p. 198–221, 6 figs.

———, 1944, Zur Kenntnis des Silurs im Rheinischen Schiefergebirge IV; Neue Fundpunkte von Tomaculum problematicum Groom im Ordovicium des Sauerlandes: Reichstelle f. Bodenforschung., Ib Bd. 63, p. 124–133.

BJØRLYKKE, K. O., 1941, Geologi, med Mineralogi og Bergartslaere. 4 ed., Oslo, p. 110, 163, 211.

BONORINO, F. G., AND TERRUGGI, M. E., 1952, Lexico sedimentologico: Instit. Nac. Investig., Publ. ext. cult. y didact., Buenos Aires, no. 6, p. 61.

BRADLEY, W. H., 1946, Coprolites from the Bridger Formation of Wyoming: Their composition and micro-organisms: Am. Jour. Sci. v. 244, p. 215–239.

BROTZEN, F., 1951, On certain phosphoritic coprolites: Geol. fören. Stockholm Förh. bd. 73, h. 4, no. 467, p. 695, illustr.

BÜLOW, K. V., 1941, Geologie für Jedermann. Kosmos, Stuttgart.

CADISCH, J., 1953, Geologie der Schweizeralpen. Basel, 480 p. (p. 203: Koprolithen an der Basis des Rhaet der Klippen-Decke.)

CAYEUX, L., 1936, Les Coprolithes des phosphates nord africains: Acad. Sci. Paris, C. R. t. 203, no. 3, p. 217–219.

COPE, E. D., 1895, On coprolites. Am. Naturalist, v. 29, p. 159.

CUVILLIER, J., 1954, Niveau a coprolithes de crustacés: Soc. géol. France, B. s. 6, t. 4, f. 1–3, p. 51–54.

DACQUE, E., 1928, Das fossile Lebewesen. Berlin, p. 26–28.

DANA-FORD, 1932, A textbook of mineralogy. 4th ed., John Wiley & Sons, Inc., New York.

DANA, J. D., 1895, Manual of geology. American Book Company New York, p. 73, 567, 754, 785, 786.

DANA, S. L., with DANA, J. F., 1845, Analysis of coprolites from the New Red Sandstone Formation of New England, with remarks by Professor Hitchcock: Am. Jour. Sci. v. 48, p. 46–60.

DEKAY, J. E., 1830a, On the remains of extinct reptiles of the genera Mosasaurus and Geosaurus found in the secondary formation of New Jersey, and on the occurrence of . . . coprolite . . . in the same locality: Lyceum Nat. History New York Annals, 3, p. 134–141.

———, 1830b, On the discovery of coprolites in North America (Cretaceous of New Jersey): Ph. Mag. n. s. 7, p. 321–322, ill.

DIETRICH, W. O., 1951, Koprolithen aus dem Pleistocän Ostafrikas. Neues Jahrb. Geol. u. Paläont., Mh. H. 10, p. 310–314.

DONZE, P., 1950, Les calcaires à coprolithes de crustacés du jurassique de la montagne des Princes et de la Chambotte (Savoie). Soc. géol. France, C. R. 7–8, p. 121–122.

EAMES, A. J., 1930, Report on ground-sloth coprolite from Dona Ana County, New Mexico: Am. Jour. Sci., 5th ser., v. 20, p. 353–356.

FIKENTSCHER, R., 1933, Koproporphyrin im tertiären Krokodilkot: Zool. Anzeiger, Bd. 103, H. 11–12, p. 289–295.

FIRTION, F., 1938, Coprolithes du lias inférieur d'Alsace et Lorraine: Alsace-Lorraine, Serv. Carte Géol., B.t. 5, p. 27–43,

GRABAU, A. W. AND SHIMER, H. W., 1910, North American index fossils: Invertebrates. v. II, A. G. Seiler & Co., New York.

GREENE, G. K., 1897, Notes on some Indiana fossils: Nat. Sci. Jour. v. 1, New Bedford, Mass., p. 29.

HITCHCOCK, E., 1844, Report on ichnolithology or fossil footmarks, with description of several new species and the coprolites of birds, and of a supposed footmark from the valley of Hudson River: Am. Jour. Sci. v. 47, p. 292–322.

HOLSER, W. T., 1947, Metasomatic processes: Econ. Geology, v. 42, p. 384–395.

HUTCHINSON, G. E., 1950, Survey of contemporary knowledge of biogeochemistry. 3. The biogeochemistry of vertebrate excretion: Am. Mus. Nat. History Bull. 96, p. 554.

KORNICKER, L. S. AND PURDY, E. G., 1957, A Bahamian faecal-pellet sediment: Jour. Sedimentary Petrology, v. 27, p. 126–128.

LADD, H. S., 1957, Treatise on marine ecology and paleoecology. Vol. 2: Paleoecology. Geol. Soc. America Memoir 67, p. 20–21.

LEA, H. C., 1843, On coprolites: Am. Philos. Soc., Pr. 3. p. 143.

LIPMAN, CH. B. AND MCLEES, E., 1940, A new species of sulferoxidizing bacteria from a coprolite: Soil Sci. v. 50, p. 429–432.

MAJOR, D. M., 1939, Origin of Washington "coprolites." The Mineralogist, Oct. 39, p. 363–364.

MAYER, G., 1952, Neue Lebensspuren aus dem unteren Hauptmuschelkalk (Trochitenkalk von Wiesloch; Coprulus oblongus n. sp. und C. sphaeroideus n. sp.) Neues Jahrb. Geol. u. Paläont., Mh. H. 8, p. 376–379.

MERRILL, G. P., 1897, Rocks, rock-weathering and soils. The Macmillan Company, New York and London, p. 152.

MORET, L., 1953, Manuel de Paléontologie animale. Paris, p. 8.

MURATA, K. T., 1940, Volcanic ash as a source of silica for the silification of wood: Am. Jour. Sci. v. 238, p. 586–596.

NEUMAYER, L., 1904, Die Koprolithen des Perms von Texas: Palaeontographica v. 51, p. 212–218.

NICHOLSON, H. A., 1889, A manual of paleontology: Vol. I, 2nd ed., H. Blackwood, London, p. 21.

NIGGLI, P., 1952, Gesteine und Minerallagerstätten. II Bd. Birkhäuser, Basel.
PARÉJAS, É., 1948, Sur quelque coprolithes de crustacés: Arch. Sci. (Soc. Phys. et His. Nat. Genève) 1, f. 3, p. 512–520.
PETTIJOHN, F. J., 1949, Sedimentary rocks. Harper and Brothers, New York.
PRICE, P. H., 1927, The coprolites limestone horizon of the Conemaugh series in and around Morgantown, West Virginia: Carnegie Mus., Annals 17, p. 211–254, 10 figs., 12 pls.
RANKAMA, K. AND SAHAMA, TH. G., 1950, Geochemistry. The University of Chicago Press, Chicago, 912 p.
RICHTER, R. UND E. RICHTER, 1939, Eine Lebens-Spur (Syncoprolus pharmaceus), gemeinsam dem rheinischen und böhmischen Ordovicium. Senckenbergiana, Bd. 21 no. 1, p. 152–167.
ROGERS, A. F., 1938, Fossil termite pellets in opalized wood from Santa Maria, Calif.: Amer .Jour. Sci., 5th ser., v. 36, p. 389–392.
SABBATONI, L., 1920, Saggi di fossilizzazione sperimentale: Soc. geol. italiana Boll. v. 39, p. 317–323.
SHROCK, R. R., 1948, Sequence in layered rocks. McGraw-Hill Book Co., Inc., New York, p. 185, 187, 304, 305.
SCHUHERT, C. AND DUNBAR, C. O., 1937, Outlines of historical geology. John Wiley and Sons, New York, p. 10.
TAKAHASHI, J.-I., 1939, Synopsis of glauconitization: Recent marine sediments. Am. Assoc. Petroleum Geologists, Tulsa. p. 503–512.
THORP, R. M., 1931, Descriptions of deep-sea bottom samples from the Western Atlantic and the Carribbean Sea: Bull. Scripps Inst. Oceanography. Tech. Ser., v. 3, p. 7–8.
TRUSHEIM, F., 1937, Eine Saurier-Mahlzeit aus dem deutschen Muschelkalk: Natur u. Volk (Senckenb. Naturf. Ges.), Bd. 67, H. 7, p. 356–358.
TWENHOFEL, W. H., 1932, Treatise on sedimentation. The Williams & Wilkins Company, Baltimore.
TWENHOFEL, W. H., AND SHROCK, R. R., 1935, Invertebrate paleontology. McGraw-Hill Book Company, Inc., New York. 511 p.
VAUGHAN, T. W., 1924, Oceanography in its relation to other earth sciences: Jour. Washington Acad. Sci., v. 14, p. 307–333.
VISSE, L. D., 1950, Note preliminaire sur les coprolithes des phosphates de l'Afrique du nord: Soc. géol. France, C. R. 7–8, p. 119–121.
WAGENBRETH, O., 1942, Auffindung eines Koprolithen aus dem Kupferschieferäquivalent bei Gera: Beitr. Geologie Thüringen Bd. 7, H. 1–2, p. 13–14.
WETMORE, A., 1943, The occurrence of feather impressions in the Miocene deposits of Maryland: The Auk, v. 60, p. 440–441.
WETZEL, W., 1937, Die koprogenen Beimengungen mariner Sedimente und ihre diagnostische und lithogenetische Bedeutung: Neues Jahrb., Beilage- Bd. 78, Abt. B., H. 1, p. 109–122.
WILLCOX, N. R., 1953, Some coprolites from phosphatic chalks in S. E. England: Annals and Mag. Nat. History Ser. 12, v. 6, p. 369–375.
WILLIAMS, H., TURNER, F. J., AND GILBERT, G. M., 1954, Petrography. W. H. Freeman and Co., San Francisco.
WOLANSKY, D., 1956, Über echte Fossilien und Pseudofossilien. Geol. Rundschau 45, p. 327–332.
WYMAN, J., 1850, On the remains of seals and a coprolite from Richmond, Virginia: Boston Soc. Nat. History Proc., v. 3, p. 323.

NOTE ADDED TO PAGE PROOF

A copy of the following new reference reached the author too late to be considered in the discussion in the foregoing paper:

ROBERTS, A. E., 1958, Geology and coal resources of the Toledo-Castle Rock district, Cowlitz and Lewis Counties, Washington: U. S. Geol. Survey Bull. 1062, p. 35–36.

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FIG. 1, DECEMBER, 1958

SETTLING TUBE FOR MECHANICAL ANALYSIS BY DECANTATION[1]

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Several types of settling tubes have been proposed to assure better separation of suspended particles by decantation during mechanical analyses.[2] A new, simple model of such a tube was designed by the writer at the University of Minnesota in 1954. Sincere appreciation is expressed to Dr. G. M. Schwartz and Dr. F. M. Swain of the University of Minnesota for their support of the study. Experience obtained since has shown that the model works well and does not require further changes.

The apparatus (fig. 1) consists of a pyrex glass cylinder about 6 cm in diameter and 17 cm high with an outlet about 3 cm in diameter which is located near the bottom of the cylinder. A double bent glass tubing is passed through a rubber cork which is plugged in the outlet. The end of the glass tubing located inside of the cylinder is shaped as a small funnel. Rubber tubing with a clamp is attached on the outside end of the glass tubing which is bent in the direction opposite to the funnel.

To calibrate the cylinder the cork in the outlet should be turned so that the funnel becomes oriented upwards. The cylinder should be filled with water and the lowermost water level "zero line" should be marked after draining the cylinder by opening the clamp. Three additional marks are made at 2.5, 5, and 10 cm above the zero mark. During the settling time the funnel should be turned upside down by a rotation of the cork. This prevents contamination by coarse particles directly precipitated into the funnel.

The described tube permits a better separation than does siphoning. By eliminating suction currents it avoids the admixture of coarser particles from the lower parts of the suspension. In addition to its use in routine mechanical analyses, the tube was successfully used for decantation of clay particles for thermodifferential and X-ray analyses, etc.

The total cost of a single specially made apparatus was about $9.00. In a simplified model, a piece of plastic tubing closed at the bottom with a rubber stopper and with a corked opening on the side may be substituted for the glass cylinder.

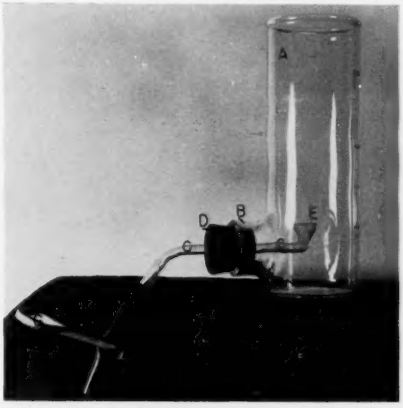

FIG. 1.—Settling tube for decantation. A—Glass cylinder; B—Outlet of the cylinder "A"; C—Double bent glass tubing; D—Rubber cork; E—Funnel shaped end of the tubing "C"; F—Rubber tubing with clamp "G."

[1] Manuscript received July 1, 1958.

[2] See Krumbein, W. C. and Pettijohn, F. J., 1938, Manual of sedimentary petrography, D. Appleton-Century Company, New York.

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DISCUSSION

PROBLEM OF THE ORIGIN OF FINE-GRAINED GYPSUM, "SUPER-INDIVIDUALS," AND SELENITE IN GYPSUM ROCK

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Little can be gained by carrying further, in print, the discussion of most of the differences between Ogniben and me (Ogniben, 1957a and b; Goldman, 1952, 1957). I would, however, like to sum up as objectively as I can the principal issue between us.

DESCRIPTION OF SUPERINDIVIDUALS

Ogniben defines "superindividual zones" as "zones with 'superindividual' polarization, i.e. with slightly differing optical orientation of the fragments" [parts]. He interprets them as rupturally deformed parts of selenite crystals (Ogniben, 1957a, p. 71, bottom of column 1).

I describe, what I believe is the same thing, as "vaguely and irregularly bounded and complexly interrelated elements" and regard them as representing stages in the growth of larger gypsum crystals from smaller ones by what I called "integration" (Goldman, 1952, p. 13), and Ogniben would call "syncrystallization" (Ogniben, 1957b, p. 469, bottom of column 1). According to Ogniben these superindividuals grade into fine-grained mylonitic gypsum and, as I understand him, all the fine-grained gypsum in his Sicilian formations except sedimentary gypsarenite (Ogniben, 1957a, p. 67, column 2, paragraph number 2), originates by crushing of selenitic or coarse crystals of gypsum.

We may be discussing different materials. Ogniben's description of the gross character of his alabastrine gypsum as "white" and "saccharoidal" (Ogniben, 1957a, p. 73, column 1) differentiates it from any cap rock gypsum I have seen, and suggests crushing. But his figure 8 in his first 1957 paper (Ogniben, 1957a, p. 72) is so strikingly like what I have interpreted as a stage in the growth of large gypsum crystals from smaller ones (Goldman, 1952, p. 13–15) that I believe it may safely be regarded as the same. His observation, also, that "there are no definite boundaries between the superindividuals. . . . No fabric analyses have been made . . . because of the continuously varying superindividual polarization" (Ogniben, 1957a, p. 73–74) corresponds with mine in the last paragraph on page 13 of my 1952 report.

The material illustrated in Ogniben's figure 8 is from his "alabastrine" gypsum. The relations illustrated from his selenitic gypsum (Ogniben, 1957a, fig. 5, p. 70) are different from anything I have seen. I therefore exclude them from the following discussion. His observation that, in selenitic gypsum, "the superindividual zones . . . start in the limpid selenite cores with zones of slight distortion of the cleavages" (Ogniben, 1957a, p. 75, bottom of column 2; *cf.* Goldman, 1952, p. 26 and especially pl. 47, fig. 3, and pl. 46, figs. 1 and 2) lends support to his interpretation of the origin of superindividuals and fine-grained gypsum by fracture. His figure 5 may therefore illustrate a different phenomenon from that illustrated in his figure 8. However, what can be seen in figure 5 does not exclude the possibility that the selenite crystal in the center grew by integration (syncrystallization) of the surrounding finer material.

ABSENCE OF ANHYDRITE IN FINE-GRAINED GYPSUM

As proof that fine-grained gypsum is not, as I regard it, an early stage in the formation of gypsum from anhydrite, but the product of crushing of large gypsum crystals, Ogniben cites the presence of remnants of anhydrite in the coarse gypsum crystals and in the superindividuals, but their absence in the fine-grained gypsum (Ogniben,

1957a and b, passim). He interprets this as indicating that large gypsum or selenite crystals developed while there were still abundant remnants of anhydrite; that, as these were broken up and crushed, water circulated in the crushed parts, the more freely the more they were crushed, gypsifying the included anhydrite. In the selenitic gypsum, and to a lesser extent in superindividuals on the other hand, the included anhydrite was protected by "the undamaged gypsum lattice" (Ogniben, 1957a, bottom of column 1).

Consider specifically the material illustrated in Ogniben's figure 10 (Ogniben, 1957a, p. 73). Ogniben says of this figure that "the fine-grained aggregates *must*" [emphasis added] "be regarded as the . . . more advanced and successive stage of transformation from anhydrite" (Ogniben, 1957b, p. 470, paragraph no. 3). However, just the opposite time sequence is possible.

Assume that, to begin with, all gypsum illustrated in that figure was fine-grained with remnants of anhydrite disseminated through it. Then superindividuals, including disseminated anhydrite, were formed from this material by integration, leaving patches or zones of fine-grained gypsum between them. The lattice of the superindividuals would then protect the included anhydrite against circulating water which would, however, dissolve the disseminated anhydrite in the fine-grained gypsum.

This interpretation seems to me preferable to Ogniben's which requires the assumption that the anastomosing zones ("vein-like patches") with coarser gypsum, which have the pattern of shear zones, are not really such, that movement in selenitic rock left these vein-like areas relatively coarse but produced the lenticular bodies of fine-grained gypsum between them by crushing the same selenitic rock. (Ogniben, 1957b, p. 470, per. 3.)

As I pointed out (1957, p. 197, column 1, last paragraph) I explain the fact that the gypsum in what I interpret as shear zones is coarser grained than that in the lenses they surround, by the effect of stress in promoting crystallization in the shear zones.

As emphasizing the complexity of the problem we are discussing, however, I want to point out that the interpretation I am suggesting for the relation of superindividual zones and fine-grained anhydrite here, does not exclude the possibility that the superindividuals, here, are the result of crushing. The gypsum in what I regard as shear zones may, after crushing by shear, have been integrated into well defined selenite crystals and have been crushed into superindividuals by later movement.

GYPSIFICATION OF ANHYDRITE

If presence or absence of anhydrite remnants can not establish the sequential relations of fine and coarse gypsum what other evidence is there?

I have illustrated (Goldman, 1952, pl. 6, fig. 2, and p. 11 and 14) small, sharply bounded gypsum crystals occupying the *undeformed* ghost of an anhydrite crystal. This was taken as evidence that the mass of fine-grained gypsum, of which these crystals were a part, had developed as such directly from anhydrite, and that it was not the product of the crushing of coarser gypsum.

INTEGRATION OF GYPSUM

To explain the presence of coarse gypsum in cap rock (e.g. Goldman, 1952, pl. 7, fig. 1) I assumed a process of integration of the small crystals into large ones. I here use integration as in my earlier paper (Goldman, 1952, p. 11 and 46) to cover the process, however it takes place. It would include Ogniben's "syncrystallization according to Rieke's principle" (Ogniben, 1957a, p. 77, column 1, second paragraph).

Ogniben regards as the product of crushing, the fine-grained gypsum that I regard as the first product of gypsification of anhydrite. He is, however, confronted (Ogniben, 1957a, p. 76, col. 2, par. 1), as I was (Goldman, 1952, p. 25, "Effect of stress on gypsum"), with the fact that no gypsum has the fine grain, range in grain size, and tattered appearance that is to be expected in mylonized material (Goldman, 1952, Index, p. 166, "Gypsum, absence of mylonization in"), and that is found, for instance, in anhydrite (cf. Goldman, 1952, pl. 48, fig. 3). I considered this indicative of the speed with which integration takes place in gypsum.

Ogniben attempts, in paragraph 5, page 470, of his 1957b paper, to account for this fact and at the same time to repudiate the assumption that coarse gypsum develops from fine gypsum. He writes:

"The absence of 'Sammelkristallisation evidence did not appear as a problem to me. 'Sammelkristallisation,' or 'syncrystallization,' should [?] take place in metamorphism or in protracted diagenesis, that is, under tectonic or load pressure and/or temperature. This could *rarely*" [emphasis added], "be the case with gypsum since it must transform in [to] anhydrite under moderate pressure (with escape of water) and temperature." Conditions that might cause the exceptions are not indicated.

This begs the entire question at issue between us. Ogniben apparently has in mind the conditions under which changes classified as metamorphic are generally believed to take place in silicate rocks. Conclusions about these conditions came from the study of silicate rocks. The conditions under which similar changes can take place in gypsum-anhydrite rock, a soluble rock of great ionic mobility (Ogniben, 1957a, p. 76, column 2, par. 1; 1957b, p. 470, top of column 2; Goldman, 1952, p. 25, second paragraph, and p. 26 bottom), must be learned from a study of that rock. It is not possible to learn whether certain changes have taken place by first stating arbitrarily, and half-heartedly at that (note "rarely" above), without any quantitative specifications, the conditions under which they "should" take place.

I have suggested that because the changes in gypsum-anhydrite rock take place under less extreme conditions of pressure and temperature, knowledge of these changes can be useful in understanding metamorphism in general (Goldman, 1952, title page and p. v–vi). It does not matter whether these changes are classified as metamorphism, prolonged diagenesis, or any other process. The issue is "Did they take place?"

Ogniben's lack of confidence in what he is trying to prove is indicated by his hedging not only in using the word "rarely" but by his invoking in the next sentence the very "Sammelkristallisation" he is trying to deny. He writes: "The only 'Sammelkristallisation' observed by me is limited to the crystalloblastic shapes of the fine-grained gypsum, in the moderate amount which is always to be expected in near-surface phenomena with such a mobile substance as gypsum." Apparently his "crystoblastic shapes" covers what I have described as "sharply defined crystals, roughly equant and with rectilinear boundaries, some of them with reentrants" (Goldman, 1952, p. 11, "Equant unintegrated gypsum" and see pl. 6, fig. 1B).

Thus Ogniben finds himself compelled to accept Sammelkristallisation to account for the absence of the ragged borders that fine-grained gypsum should have if it were the product of crushing; but he wants just enough to meet that requirement and no more.

By invoking the ready solubility and ionic mobility of gypsum in explaining the absence of mylonized gypsum, Ogniben makes it all the more difficult to accept his conclusion that integration stops where he would have it stop.

ORIGIN OF SELENITE IN SICILIAN GYPSUM ROCK

Ogniben derives gypsum rock, other than gypsarenites, from anhydrite rock (Ogniben, 1957a, p. 71, column 2, first paragraph) and on this we are entirely in agreement (Goldman, 1925, p. 43; 1926, p. 51, and fig. 6; 1952, p. 10). He apparently assumes that the direct result of this derivation was selenite and that "superindividuals" and fine-grained gypsum are the products of stress acting on the selenite so derived.

But if these selenite crystals did not form by integration (syncrystallization) of finer grained gypsum their origin seems to me to present a problem for which Ogniben offers no solution.

I find it difficult to conceive of the *direct* formation of large selenite crystals from a mass of randomly oriented anhydrite crystals. If a growing crystal of gypsum advances into such a mass along a fairly solid continuous front it is quite conceivable that the added gypsum would assume the crystallographic orientation of the advancing gypsum crystal (see, for example, Goldman, 1952, pl. 14, fig. 5B). But in a mass of fine-grained anhydrite, especially if it has been stressed, it seems more likely that gypsification would start at several centers with independent crystallographic orientation of the gypsum at each center. To derive single large, selenite crystals from such an assemblage would require some sort of integration.

Previously, in trying to raise the question of the origin of the selenite crystals which

Ogniben illustrates, and from which he derives superindividuals and fine-grained aggragates, I mistakenly formulated the question so as to imply that the selenite crystals must be derived by integration from small gypsum crystals. For "Sammelkristallisation of the type defined by Rinne" (Goldman, 1957, p. 197, col. 2, paragraph 2) I should have written "origin of selenite crystals" (by any process).

However, Ogniben's reply (1957b, p. 470, col. 2, par. 1), involving the basic difference of interpretation between us, is also misleading. He writes: "No stages of grading from fine-grained aggregates to large clear gypsum crystals were observed for the simple reason that this process did not take place in Sicilian Upper Miocene gypsum. Only the opposite process occurred as is illustrated especially by my figures 5 and 6 (Ogniben, 1957a)." So far as I can find any evidence in his two papers, all he can say is that he does not *conceive* of the sequential relations as being from fine to coarse, only the opposite.

The same criticism applies to an earlier statement by Ogniben: "Since limpid crystals, superindividuals and fine size aggregates have been *seen*" [emphasis added] "as successive stages in the destructive sense . . ." (Ogniben, 1957*a*, p. 77, col. 2, par. 1).

In both these quotations interpretation is confused with observation. The second statement, not derivation of gypsum from anhydrite (Ogniben, 1957*b*, p. 470, par. 6) is what I had in mind when I wrote "neither of us has seen any transformation actually take place" (Goldman, 1957, p. 197, col. 2, par. 3). The "successive *deformational* [emphasis added] stages" are purely an interpretation, as is my opposite assumption that they are stages of growth. The process by which the selenite crystals in Sicilian gypsum rock originated from anhydrite has not been described or illustrated and seems to me to require explanation.

In relation to that problem Ogniben's statement that "Most anhydrite is of the type known as 'regenerated anhydrite' " (Ogniben, 1957a, p. 67, col. 2, last paragraph) may be significant. He has mistakenly stated (Ogniben, 1957b, p. 469, last paragraph) that I did not find selenitic gypsum. Much of the gypsum containing regenerated anhydrite that I studied is in pure, clear, undeformed crystals (Goldman, 1952, p. 65, par. 16 and e.g. pl. 54). I have mentioned a 2 inch × 2½ inch piece of core of what appears to be a single selenite crystal, from a depth of about 1069 feet, closely associated with a regenerated specimen (Goldman, 1952, p. 13, seventh paragraph, p. 26, top). I have attributed this selenitic gypsum associated with regenerated anhydrite to more complete integration due to greater age.

REFERENCES

GOLDMAN, MARCUS I., 1925, Petrography of salt dome cap rock: Am. Assoc. Petroleum Geologists Bull., v. 9, p. 42–78.

———, 1926, Same paper, *in* Geology of salt dome oil fields: Am. Assoc. Petroleum Geologists, p. 50–86.

———, 1952, Deformation, metamorphism and mineralization in gypsum-anhydrite cap rock: Geol. Soc. America, Memoir 50.

———, 1957, Relations of gypsum and anhydrite: Jour. Sedimentary Petrology, v. 27, p. 196–197.

OGNIBEN, LEO, 1957a, Secondary gypsum of the Sulphur Series, Sicily, and the so-called integration: Jour. Sedimentary Petrology, v. 27, p. 64–79.

———, 1957b, Relations of gypsum and anhydrite: Jour. Sedimentary Petrology, v. 27, p. 469–470.

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DISCUSSION

"DOLOSTONE"

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The standardization of sedimentary rock nomenclature is becoming a serious and pressing matter. Neologisms continue to multiply at an alarming rate, and we are surely heading for another Tower of Babel. Some sort of international agreement is urgent.

Many of the newly-coined terms are inappropriate, ambiguous and badly constructed. "Dolostone" is typical. Proposed in 1948 by Schrock, it has recently been adopted in a major text-book (Dunbar & Rodgers 1957). Admittedly there are grounds here for inventing a new English word, since "dolomite" denotes both mineral and rock. But "dolostone" is quite unacceptable. If the English root "stone" is used then the word should strictly be "dolomieustone." But this is difficult to pronounce. Nor can the regrettable modern tendency to incorporate abbreviations into new terms excuse the drastic truncation of Dolomieu's name. Surely this mineralogist-nobleman, a survivor of the guillotine from the Revolution, hardly deserves such a fate! Other mineral species, often bearing longer patronomic names, are not normally decapitated in this brutal fashion.

But that is not an end to it. Innocents, trying to work out the meaning of "dolostone" from its etymology, are liable to draw some strange conclusions:

1. There is a small Venetian town called "Dolo." Is this the type locality?
2. In jurisprudence in the Latin and Greek languages the same root means "fraud" or "deceit" (Latin *dolis*, Italian and Spanish *dolo*, Greek *dolos*). English law also employes the same form (dolose) with a similar meaning. Dolomite-rocks are admittedly often deceitful, but this is hardly likely to be the meaning intended!

At the risk of being accused of chauvinism, I must point out that the terms "dolomie" for the rock (de Saussure 1792) and "dolomite" for the mineral (Kirwan 1794) already avoid these difficulties. The termination "ie" is not often used in English. But its adoption might well prove advantageous.

I thank Professor P. Allen for translating the text of this discussion into English.

REFERENCES

DE SAUSSURE, N. T., 1792, Analyse de la dolomie: Jour. dephysique, tome 40, p. 161–173.
DUNBAR, C. V., AND RODGERS, J., 1957, Principles of stratigraphy. John Wiley and Sons, Inc., New York, 356 p.
KIRWAN, R., 1794, Elements of mineralogy. 2nd ed., v. 1, London.
SCHROCK, R. R., 1948, A classification of sedimentary rocks: Jour. Geology, v. 5, p. 118–129.

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NOTE

MODIFICATION OF UNDERWATER SURFACE SEDIMENT LAYERS BY SEA MUSSELS (*MYTILUS EDULIS*)[1]

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Kingston, Rhode Island

A study of a field sample collected during August 1955 by free-swimming divers revealed an interesting relationship between living sea mussels (*Mytilus edulis* L.) and the bottom sediments. The sample was obtained during a project sponsored by the Office of Naval Research concerning sedimentary processes in southern New England coastal waters. It was taken in 37 feet of water on the east side of Quicks Hole, a narrow passage between Nashawena and Pasque Islands, in the Elizabeth Island chain off the southern coast of Massachusetts. In this area, the bottom was found to be generally level but the interface was rough due to the presence of numerous cobbles, pebbles, and shells. High-velocity, semidiurnal, reversing tidal currents swept the bottom which, for the most part, was composed of gravel, sand, and admixtures of these components. During the period of observation, the bottom was almost completely covered with living mussels except for a few small patches of exposed coarse particles. In addition, a maximum current of two knots was measured two feet above the bottom and the current velocity exceeded 1.8 knots for one and a half hours continuously.

Although a mussel-covered sea bottom in itself is certainly not unusual, a detailed examination of the present bottom sample (4×9×4 inches) revealed several significant facts about the shellfish-sediment interface. At the surface, living mussels which measured from ½ to ¾ inch in length and which were probably less than one year old (Field, 1922 p. 162) were attached at their anterior ends to an underlying, poorly-sorted, gravelly sand. Their posterior or siphon ends project vertically into the water mass. As far as could be determined, there was no preferred alignment of the animals' body axes with the direction of current flow and there was no evidence of successive sets overlying one another. However, the mode and tenacity of attachment to the underlying sediment was of particular interest. These animals were not just anchored by their secreted byssal threads to particles exposed along the bottom surface, but apparently many of these tough threads had penetrated into the sediment, thus securing the mussels to various-sized particles throughout the upper portion of sediment. The tenacity and thoroughness of attachment to the grains was such that the top one inch of sediment constituted a flexible mat of tightly-bound, heterogeneous particles and could be peeled off intact with its mussel cover.

In order to gain an understanding of this phenomenon, it is necessary to review briefly several pertinent facts concerning the sea mussel's foot and byssus. (1) The tongue-like foot serves as an organ of locomotion and, in conjunction with the glands of the byssus cavity, it also functions in producing the byssal material and attaching threads to favorable objects. (2) Vigorous environmental conditions in the form of stresses which the byssus has to withstand probably stimulate a more rapid secretion of byssal material. Such stimulated growth is capable of producing threads of cumbersome lengths but the shellfish is able to minimize this by releasing the threads at will and starting new ones (Field, 1922, p. 161). (3) Apparently, these animals move along the bottom by alternately securing new threads forward and casting off old ones behind (Williamson, 1907). (4) It is possible for a young mussel to extend its foot a distance beyond its base nearly equal to the length of the animal itself (Field, 1922, p. 161).

[1] Contribution No. 20 from the Narragansett Marine Laboratory. Manuscript received October 6, 1958.

Undoubtedly, the rigorous nature of the Quicks Hole environment not only subjects the byssus to heavy stress, but the animal must also obtain as many anchors as possible if it is to survive the effects of bottom current agitation. Each animal must, in order to maintain adequate holding power, repeatedly burrow its foot into the loose sediment to secure additional anchors throughout the range of its foot extension. As a result of this process, numerous threads apparently tie together the grains in the surface sediment layers to form a natural mat.

It is believed that this condition must provide an effective protection against submarine erosion in this local environment. By immobilizing the surface sediment grains, especially the medium and fine sand sizes, against movement due to current velocity or turbulence, the bottom surface is effectively stabilized. After the mussel bed has died, presumably the remaining threads will continue to bind the surface sediment layers for a period of some duration, perhaps until a new set occurs. It would be interesting to know how long this condition persists.

REFERENCES

FIELD, I. A., 1922, Biology and economic value of the sea mussel *Mytilus edulis;* Bull. Bur. Fish., v. 38, p. 127–259.

WILLIAMSON, H. C., 1907, The spawning, growth, and movement of the mussel (*Mytilus edulis*, L.) horse-mussel (*Modiolus modiolus*, L.), and the spoutfish (*Solen siliqua*, L.) 25th Ann. Rept. Fish. Bd. Scotland 1906, Pt. 3, p. 221–255.

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ANNOUNCEMENTS

SOCIETY OF ECONOMIC PALEONTOLOGISTS AND MINERALOGISTS PERMIAN BASIN SECTION

PRELIMINARY ANNOUNCEMENT OF ANNUAL MEETING AND FIELD TRIP TO BE HELD AT ROSWELL, NEW MEXICO, APRIL 2, 3, 4, 1959

The annual technical and business meetings of the Permian Basin Section, Society of Economic Paleontologists and Mineralogists will be held Thursday, April 2, 1959, in Roswell, New Mexico. General Chairman is M. Russell Stipp, Standard Oil Company of Texas, Box 746, Roswell, New Mexico. Chairman of the technical program is Richard F. Meyer, Humble Oil and Refining Company, Box 1287, Roswell, New Mexico.

A field trip in the area of the Sacramento Mountains, New Mexico, is planned for Friday and Saturday, April 3 and 4, 1959. General Chairman is Carl Ulvog, Sunray Mid-Continent Oil Company, Wilco Building, Midland, Texas. Details of the trip will be announced later.

SOCIETY OF ECONOMIC PALEONTOLOGISTS AND MINERALOGISTS SYMPOSIUM, ATLANTIC CITY, 1960

The Paleontological and Mineralogical Aspects of Polar Wandering and Continental Drift

Just thirty years ago the A.A.P.G. conducted a symposium on the theory of continental drift. This was attended by many experts and by supporters of the Wegener hypothesis. Although many of our minds were then set at rest, developments in the past four years necessitate that the subject be reconsidered and re-evaluated. Accordingly, the Executive Committee has planned a full day symposium and an evening open forum discussion on this subject that should create great interest among our members.

Those interested are invited to contact the chairman, Dr. Arthur C. Munyan, Vice Chairman, Research Committee, S.E.P.M., Sohio Petroleum Company, P. O. Box 2558, Billings, Montana.

XXIST INTERNATIONAL GEOLOGICAL CONGRESS NORDIC COUNTRIES, AUGUST 1960 FIRST CIRCULAR

Copies of the First Circular for the 21st IGC may be obtained on request from the *American Geological Institute, 2101 Constitution Avenue, N. W., Washington 25, D. C.* Names of all persons requesting the First Circular will be placed on a list to receive travel literature and other pertinent information.

BIBLIOGRAPHY AND INDEX OF LITERATURE ON URANIUM AND THORIUM AND RADIOACTIVE OCCURRENCES IN THE UNITED STATES. PARTS 1–5

The Geological Society of America has published as its Special Paper No. 67, "Bibliography and Index of Literature on Uranium and Thorium and Radioactive Occurrences in the United States. Part 5: Connecticut, Delaware, Illinois, Indiana, Maine, Maryland, Massachusetts, Michigan, New Hampshire, New Jersey, New York, Ohio, Pennsylvania, Rhode Island, Vermont, and Wisconsin," prepared by Margaret Cooper of the U. S. Geological Survey on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission, September 1958, 472 pages (paper cover), and priced at $6.75 a copy.

This book contains a section on bibliography (26 pages), a gazetteer for the States (38 pages), a geographical index (243 pages), and a subject index (165 pages). Factually it is a key to the literature on deposits in which uranium, thorium, and radioactive minerals are found in the northeastern United States. For many of the States there is also much detailed information in the indexes on the geology and the general mineralogy of the pegmatites, coal beds, sandstones, shales, beach sands, and other formations in which the uranium and thorium have been reported.

Parts 1 to 4 of this bibliography were prepared by Margaret Cooper in the Division of Raw Materials of the U. S. Atomic Energy Commission and published in the Bulletin of the Society. These sections, which also include a bibliography, gazetteer, geographical index, and subject index, with detailed geological information for each area covered, are available as reprints for public sale, as follows:

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Journal of Sedimentary Petrology

INDEX TO VOLUME 28

A defense of the term alterite 234
Aeolian microenvironments by mechanical composition, Differention of various Egyptian 164
Alberta, Sedimentary "boudinage" structures in the Upper Devonian Ireton Formation of 316
Alkali metals in some Gulf of Mexico sediments, Occurrence of 431
Alteration of volcanic ash near Denver, Colorado 31
Alterite, A defense of the term 234
Amstutz, G. C., article by 498
Announcements 112, 241, 517–518
An occurrence of flat-topped ripple marks 95
A statistical study of heavy minerals in sands of the South River, Augusta County, Virginia 111
Aurèle La Rocque, The Admirable Discourses of Bernard Palissy, review of. 379

Banded iron formations, Fresh-water environment of deposition of Precambrian 414
Barrier islands in panhandle Florida, Possible abandoned 342
Bauxite-clay-iron oxide ore, Proposed classification and terminology of rocks in the series 93
Beals, H. O., article by 233
Beaumont Clay, Size distributions of zircon grains in some samples of the lower .. 36
Berry, W. B. N., article by 389
Bissell, H. J., article by 490
Boucot, A. J., article by 321
Bottom sediments of southern part of Pyramid Lake, Nevada 286
"Boudinage" structures in the Upper Devonian Ireton Formation of Alberta, Sedimentary 316
Brace, W., article by 321
Brachiopod and pelecypod shells by currents, Distribution of 321
Brenneman, L., article by 242
Briggs, L. I., article by 46
Briggs, L. I., errata by 384
British Upper Carboniferous shales, Preliminary observations on chemical data for some 209
Bryozoan core facies, Mississippian bioherms, southwestern United States, Fenestrate 261
Buerger, M. J., "Elementary Crystallography," review of 237

Calcium carbonate in the shelf sediments off east coast of India, Distribution of 274
Carozzi, A. V., article by 133
Carozzi, A. V., review by 240
Carroll, D., errata by 111
Chayes, F., "Petrographic Modal Analysis" review of 236
"Chemistry in Introductory Geology," review of 240
Chert in the Middle Ordovician Hardy Limestone of Southwest Virginia, Syngenetic 205
Chilingar, G. V., article by 490
Classification and terminology of rocks in the series bauxite-clay-iron oxide ore, Proposed 93
Clay accumulation, Tidal action as the cause of 406
Clay mineral composition of Recent sediments from the Mississippi River Delta 186
Colorado, Alteration of volcanic ash near Denver 31
Comments on "Some apparently misunderstood aspects concerning stylolites" 378
Comparison of phi percentile deviations 203
Concretion, Rate of formation of a diagenetic calcareous 366
Coprolites: a review of the literature and a study of specimens from southern Washington 498
Core facies, Mississippian bioherms, southwestern United States, Fenestrate bryozoan 261
Corer for use in shallow water, Description of a portable piston 227
Corrosion zones: a modified hypothesis of their origin 486
Cow Run Sand, St. Marys, West Virginia, Petrography and porosity of 15
Cropp, F., article by 102
Currents, Distribution of brachiopod and pelecypod shells by 321
Cyclic deposition in the Jrasssic Carmel Formation of eastern Utah 40
Cyclic patterns in mechanically deposited Pennsylvanian limestones of northeastern Nevada 3

Davis, S. N., article by 87
Dawson, R. E., article by 361
Decantation, Settling tube for mechanical analysis by 509
DeMar, R., article by 321
Denver, Colorado, Alteration of volcanic ash near 31
Depositional environment of the Ordovician succession in the Marathon region, Texas 389
Depositional environment, Probability curves and the recognition of adjustment to 151
Description of a portable piston corer for use in shallow water 227
Detrital and non-detrital fractions of limestones, Techniques of sedimentary geochemistry: (1) separation of the 468
Diagenetic dolomitization, Notes on 490
"Die Quarzkornfarbe als Hilfsmittel für die stratigraphische und Paläogeographis-

che Erforschung sandiger Sedimente and Die Lithologie und Paläogeographie des Buntsandsteins am Westrand der Böhmischen Masse," review of ... 240
Differentiation of beach, dune, and aeolian flat environments by size analysis, Mustang Island, Texas ... 211
Differentiation of various Egyptian aeolian microenvironments by mechanical composition ... 164
Dip direction indicator ... 230
Displacement of microfossils ... 453
Distribution of calcium carbonate in the shelf sediments off east coast of India 274
Dolomitization, Notes on diagenetic ... 490
"Dolostone" ... 514
Dott, Jr., R. H., article by ... 3
Droste, J. B., article by ... 345
Dunbar, C. O. and Rodgers, J., "Principles of Stratigraphy," review of ... 237

Egyptian aeolian microenvironments by mechanical composition, Differentiation of various ... 164
Electron micrography of till matrix ... 345
"Elementary Crystallography," review of . 237
Environment along the coast of panhandle Florida, Roundness as an indicator of 351
Epicontinental environment, Micro-mechanisms of sedimentation in the ... 133
Etching technique for use on thin sections of limestones ... 200
Evaporite facies ... 46

Fenestrate bryozoan core facies, Mississippian bioherms, southwestern United States ... 261
Fifth International Congress of Sedimentology ... 112
Florida, Possible abandoned barrier islands in panhandle ... 342
Florida, Roundness as an indicator of environment along the coast of panhandle 351
Florida, Sedimentary analysis of terrace deposits in panhandle ... 75
Folk, R. L., article by ... 211
Fresh-water environment of deposition of Precambrian banded iron formations 414

Garrels, R. M., review by ... 240
Geochemistry: (1) separation of the detrital and non-detrital fractions of limestones, Techniques of sedimentary ... 468
Geological studies on the Great Bahama Bank, errata ... 111
"Geologic Field Methods," review of ... 238
Glacial till, Size distribution of rock types in stream gravel and ... 87
Goldman, M. I., discussion by ... 510
Great Slave Lake, Northwest Territories, Recent grooving in lake bottom sediments at ... 333
Green, K. E., article by ... 227
Greensmith, J. T., article by ... 209
Greywacke Series, Two uncescribed structures in a ... 97
Griffiths, J. C., article by ... 15
Grim, R. E., article by ... 186
Gulf of Mexico sediments, Occurrence of alkali metals in some ... 431
Gypsum, "Superindividuals," and selenite in gypsum rock, Problem of the origin of fine-grained ... 510

Hardy Creek Limestone of southwest Virginia, Syngenetic chert in the Middle Ordovician ... 205
Harris, L. D., article by ... 205
Harris, S. A., articles by ... 151, 164
Heavy mineral variation in San Antonio and Mesquite Bays of the central Texas coast ... 65
Henderson, D. M., review by ... 237
Hirst, D. M., article by ... 468
Hough, J. L., articles by ... 102, 414

India, Distribution of calcium carbonate in the shelf sediments off coast of ... 274
"Introduction to Microfossils," review of . 239
Ireton Formation of Alberta, Sedimentary "boudinage" structures in the Upper Devonian ... 316
Iron formations, Fresh-water environment of deposition of Precambrian banded 414

Johns, W. D., article by ... 186
Jones, D. J., article by ... 453
Jones, D. J., "Introduction to Microfossils", review of ... 239
Journal of Sedimentary Petrology, Rules and suggestions for preparation of manuscripts for the ... 102
Jurassic Carmel Formation of eastern Utah, Cyclic deposition in the ... 40

Keller, W. D., "Chemistry in Introductory Geology," review of ... 240
Konta, J., article by ... 93
Krumbein, W. C., article by ... 175
Kuenen, Ph. H., article by ... 406

Lake bottom sediments at Great Slave Lake, Northwest Territories, Recent grooving in ... 333
Lapinsky, W. J., article by ... 75
Lees, A., article by ... 200
Limestones, Etching technique for use on thin sections of ... 200
Limestones, Techniques of sedimentary geochemistry: (1) separation of the detrital and non-detrital fractions of 468
Lissie Formation, Size distribution of zircon and tourmaline grains in some samples of the ... 361
Low, J. W., "Geologic Field Methods," review of ... 238

Manuscripts for the *Journal of Sedimentary Petrology*, Rules and suggestions for the preparation of ... 102
Marathon region, Texas, Depositional environment of the Ordovician succession in the ... 389
Marine salts from sediment samples, Rapid removal of ... 231

Mason, C. C., article by 211
Mass movements in Permian rocks of Trans-Pecos Texas 298
McAllister, R. F., article by 231
McCrossan, R. G., article by 316
McMaster, R. L., note by 515
Meader, R. W., article by 286
Measurement and error in regional stratigraphic analysis 175
Mechanically deposited Pennsylvania limestones of northeastern Nevada, Cyclic patterns in 3
Membership list, S.E.P.M. 115
Merrill, W. M., review by 238
Mesquite Bays of the central Texas coast, Heavy mineral variation in San Antonio and 65
Metals in some Gulf of Mexico sediments, Occurrence of alkali 431
Microenvironments by mechanical composition, Differentiation of various Egyptian aeolian 164
Microfossils, Displacement of 453
Micro-mechanisms of sedimentation in the epicontinental environment 133
Miller, R. L., review by 236
Mississippian bioherms, southwestern United States, Fenestrate bryozoan core facies 261
Mississippi River Delta, Clay mineral composition of recent sediments from the 186
Modification of underwater surface sediment layers by sea mussels (*Mytilus edulis*) 515
Mussels (*Mytilus edulis*), Modification of underwater surface sediment layers by sea 515
Mustang Island, Texas, Differentiation of beach, dune, and aeolian flat environments by size analysis 211
(*Mytilus edulis*), Modification of underwater surface sediment layers by sea mussels 515

Nairn, A. E. M., article by 57
Nevada, Bottom sediments of southern part of Pyramid Lake 286
Nevada, Cyclic patterns in mechanically deposited Pennsylvanian limestones of northeastern 3
New abrasive for sectioning water-soluble rocks 233
Newell, N. D., errata by 111
New technique for measuring roundness of sand grains 108
Nicholls, C. D., article by 468
Northwest Territories, Recent grooving in lake bottom sediments at Great Slave Lake 333
Notes on diagenetic dolomitization 490

Occurrence of alkali metals in some Gulf of Mexico sediments 431
Occurrence of flat-topped ripple marks, An 95
Ogniben, L., errata by 111
Ordovician Hardy Creek Limestone of southwest Virginia, Syngenetic chert in the Middle 205
Ordovician succession in the Marathon region, Texas, Depositional environment of the 389

Panhandle Florida, Sedimentary analysis of terrace deposits in 75
Pantin, H. M., article by 366
Patterns in mechanically deposited Pennsylvanian limestones of northeastern Nevada, Cyclic 3
Pelecypod shells by currents, Distribution of brachiopod and 321
Pennsylvanian Limestones of northeastern Nevada, Cyclic patterns in mechanically deposited 3
Permian Basin Section Field Trip, 1958 112
Permian Basin Section Field Trip, 1959 517
Permian rocks of Trans-Pecos Texas, Mass movements in 298
"Petrographic Modal Analysis," review of 236
Petrography and porosity of the Cow Run Sand, St. Marys, West Virginia 15
Petrology of the Whita Sandstone, southern Scotland 57
Pettijohn F. J., note by 378
Phi percentile deviations, Comparison of 203
Poole, D. M., article by 65
Porosity of the Cow Run Sand, St. Marys, West Virginia, Petrography and 15
Possible abandoned barrier islands in panhandle Florida 342
Powell, W. F., article by 36
Pray, L. C., article by 261
Precambrian banded iron formations, Fresh-water environment of deposition of 414
Preliminary observations on chemical data from some British Upper Carboniferous shales 209
"Principles of Stratigraphy," review of 237
Probability curves and the recognition of adjustment to depositional environment 151
Problem of the origin of fine-grained gypsum, "Superindividuals," and selenite in gypsum rock 510
Program for S.E.P.M., Los Angeles meeting 113
Prokopovich, N., article by 509
Proposed classification and terminology of rocks in the series bauxite-clay-iron oxide ore 93
Pryor, W., article by 230
Publication of a French Translation, "Les Methodes d'Etude des Roches sedimentaries," of a Russian Symposium on the Methods of Study of Sedimentary Rocks 241

Rao, M. S., article by 274
Rapid removal of marine salts from sediment samples 231
Rate of formation of a diagenetic calcareous concretion 366
Recent grooving in lake bottom sediments at Great Slave Lake, Northwest Territories 333
Recent sediments from the Mississippi River Delta, Clay mineral composition of 186

Reish, D. J., article by 227
Relations of gypsum and anhydrite 111
Revell, S. R., article by 75
Richards, H. G., article by 40
Rigby, J. K., article by 298
Rigby, J. K., errata by 111
Ripple marks, An occurrence of flat-topped 95
Robson, D. A., note by 108
Rock types in stream gravel and glacial till, Size distribution of 87
Rogers, J. J. W., articles by 36, 361
Roundness as an indicator of environment along the coast of panhandle Florida 351
Roundness of sand grains, New technique for measuring 108
Rules and suggestions for preparation of manuscripts for the *Journal of Sedimentary Petrology* 102

San Antonio and Mesquite Bays of the central Texas coast, Heavy mineral variation in 65
Schlocker, J., article by 15
Schnitzer, W. A., "Die Quarzkornfarbe als Hilfsmittel für die stratigraphische und Paläogeographische Erforschung sandiger Sedimente and Die Lithologie und Paläogeographie des Buntsandsteins am Westrand der Böhmischen Masse," review of 240
Scotland, Petrology of the Whita Sandstone, southern 57
Scott, H. W., reviews by 237, 239
Sectioning water-soluble rocks, New abrasive for 233
Sedimentary analysis of terrace deposits in panhandle Florida 75
Sedimentary "boundinage" structures in the Upper Devonian Ireton Formation of Alberta 316
Sedimentation in the epicontinental environment, Micro-mechanisms of 133
Sediment samples, Rapid removal of marine salts from 231
Selenite in gypsum rock, Problem of the origin of fine-grained gypsum, "Superindividuals," and 510
Settling tube for mechanical analysis by decantation 509
Seventh National Conference on Clays 241
Shaub, B. M., note by 376
Shelf sediments off coast of India, Distribution of calcium carbonate in the 274
Shepps, V. C., article by 482
Size analysis, Mustang, Island, Texas, Differentiation of beach, dune, and aeolian flat environments by 211
Size distribution of rock types in stream gravel and glacial till 87
Size distribution of zircon and tourmaline grains in some samples of the Lissie Formation 361
Size distributions of zircon grains in some samples of the lower Beaumont Clay 36
"Size Factors," a means of analysis of data from textural studies of till 482
Smith, A. J., article by 97
Society of Economic Paleontologists and Mineralogists
Membership List 115
Program for S.E.P.M. Los Angeles meeting 113
Records and Activities 242, 381
Some apparently misunderstood aspects concerning stylolites 376
St. Marys, West Virginia, Petrography and porosity of the Cow Run Sand of 15
Straaten, L. M. J. U. van, article by 406
Stratigraphic analysis, Measurement and error in regional 175
Stream gravel and glacial till, Size distribution of rock types in 87
Stylolites, Comments on "Some apparently misunderstood aspects concerning stylolites" 378
Stylolites, Some apparently misunderstood aspects concerning 376
Surface sediment layers, modification of, by sea mussels (*Mytilus edulis*) 515
Suggestions for preparation of manuscripts for the *Journal of Sedimentary Petrology*, Rules and 102
"Superindividuals," and selenite in gypsum rock, Problem of the origin of fine-grained gypsum 510
Swain, F. M., article by 286
Syngenetic chert in the Middle Ordovician Hardy Creek Limestone of southwest Virginia 205

Tanner, W. F., articles by 95, 203, 342, 372
Techniques of sedimentary geochemistry: (1) separation of the detrital and nondetrital fractions of limestones 468
Terminology of rocks in the series bauxite-clay-iron oxide ore, Proposed classification and 93
Terrace deposits in panhandle Florida, Sedimentary analysis of 75
Texas coast, Heavy mineral variation in San Antonio and Mesquite Bays of the central 65
Texas, Depositional environment of the Ordovician succession in the Marathon region 389
Texas, Differentiation of beach, dune, and aeolian flat environments by size analysis, Mustang Island 211
Texas, Mass movements in Permian rocks of Trans-Pecos 298
"The Admirable Discourses of Bernard Palissy," review of 379
The zig-zag nature of type I and type IV curves 372
Thin sections of limestone, Etching technique for use on 200
Thompson, H. R. review by 370
Tidal action as the cause of clay accumulation 406
Till matrix, Electron micrography of 345
Till, "Size factors," as means of analysis of data from textural studies of 482
Tourmaline grains in some samples of the Lissie Formation, Size distribution of zircon and 361
Two undescribed structures in a greywacke series 97

Utah, Cyclic deposition in the Jurassic Carmel Formation of eastern 40

van Andel, T. H., discussion by 234
Van Horn, R., article by 31
van Straaten, L. M. J. U., article by 406
Vatan, A., discussion by 514
Vatter, A. E., article by 345
Virginia, Syngenetic chert in the Middle Ordovician Hardy Creek Limestone of southwest 205
Volcanic ash near Denver, Colorado, Alteration of 31

Washington, Coprolites: a review of the literature and a study of specimens from southern 498
Waskom, J. D., article by 351
Weber, J. N., article by 333
Weiss, M. P., article by 486
Welby, C. W., article by 431
West Virginia, Petrography and porosity of the Cow Run Sand, St. Marys 15
Whita Sandstone, southern Scotland, Petrology of the 57
White G. W., article by 345
Winters, S. S., article by 75
Wood, A., article by 97

Zig-zag nature of type I and type IV curves, The 372
Zircon and tourmaline grains in some samples of the Lissie Formation, Size distribution of 361
Zircon grains in some samples of the lower Beaumont Clay, Size distribution of 36

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Vol. 9 (1935), Nos. 1,2,3,4,5,6,7,8
Vol. 10 (1936), Nos. 1,2,3,4,5,6,7,8
Vol. 11 (1937), Nos. 1,2,3,4,5,6,7,8
Vol. 12 (1938), Nos. 3,4,5,6
Vol. 13 (1939), Nos. 1,2,3,4,5,6
Vol. 14 (1940), Nos. 1,2,3,4,5,6
Vol. 15 (1941), Nos. 1,2,3,4,5,6
Vol. 16 (1942), Nos. 1,2,3,4,5,6
Vol. 17 (1943), Nos. 1,2,3,4,5,6
Vol. 18 (1944), Nos. 1,2,3,4,5,6
Vol. 19 (1945), Nos. 1,2,3,4,5,6
Vol. 21 (1947), Nos. 3,4,5,6
Vol. 22 (1948), Nos. 3,4,5,6
Vol. 24 (1950), Nos. 2,3,4,5,6
Vol. 25 (1951), Nos. 3,4,5,6
Vol. 26 (1952), Nos. 3,4,5,6
Vol. 27 (1953), Nos. 1,2,3,4,5,6
Vol. 28 (1954), Nos. 1,2,3,4,5,6
Vol. 29 (1955), Nos. 1,2,3,4,5,6
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Vol. 1 (1931), No. 2
Vol. 2 (1932), Nos. 1,2,3
Vol. 3 (1933), Nos. 1,2,3
Vol. 4 (1934), No. 3
Vol. 5 (1935), Nos. 1,2
Vol. 20 (1950), Nos. 1,2,3,4
Vol. 21 (1951), No. 1
Vol. 22 (1952), Nos. 1,2,3,4
Vol. 23 (1953), Nos. 1,2,3,4
Vol. 24 (1954), No. 4
Vol. 25 (1955), Nos. 1,2,3,4
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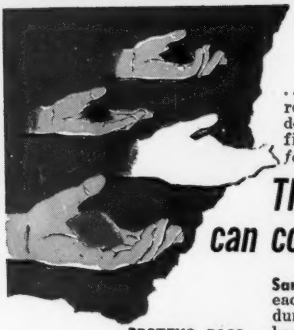

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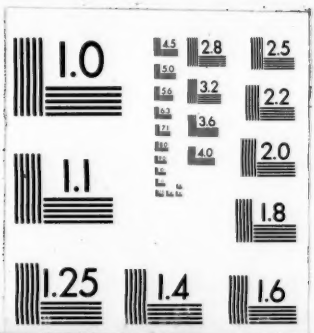
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